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Field Demonstration for Mobile FT-IR for Detection of Volatile Organic Chemicals

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FIELD DEMONSTRATION FOR MOBILE FT-IR FOR DETECTION OF VOLATILE ORGANIC CHEMICALS

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16. ABSTRACT

A mobile laboratory is now available to measure toxic compounds in the atmosphere. The mobility of this unit allows access to many sites in the continental United States. When this laboratory arrives at a designated site, a high resolution Fourier transform (FT-IR) instrument is used to measure the toxic materials, or volatile organic compounds, in the atmosphere. The site could be a landfill, lagoon, industrial site, chemical spill or any area where atmospheric pollution occurs. The FT-IR instrument is capable of identifying and quantifying atmospheric molecules at the parts per billion (ppb) level. The path observed by this instrument could be as small as a few meters, or as large as 600 meters in length, nearly 2,000 feet. Recently, the chemicals emitted at an industrial site have been identified at distances of up to 0.3 mile.

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ABSTRACT

A mobile laboratory for on-site analyses of volatile organic compounds (VOCs) in the atmosphere using a Fourier transform infrared (FT-IR) spectrometer is described. Laboratory calibration measurements are presented and discussed. Estimates of detection limits as an average concentration over a path length of 100 meters are made for 26 mid-infrared absorption bands of 21 compounds. These estimated detection limits vary from 5 to 76 parts per billion (ppb). Some results of field measurements carried out at path-lengths near 100 meters are presented and discussed. Field measurements at a number of path lengths up to 600 m at an industrial site are presented.

Included in this report is a small collection of uncalibrated reference spectra. These spectra have been added to Appendix 3 because they are part of our spectral library.

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ABBREVIATIONS AND SYMBOLS

A	Absorbance ($\log_{10} (T_0/T)$ where T_0 is background transmittance and T is sample transmittance) in Beer's Law
A_m	Minimum detectable absorbance
APER	Aperture for light stop
APOD	Apodization
A_r	Absorbance in calibration spectrum recorded at the lovest concentration
a	Absorption coefficient in Beer's Law
Beer's Law	A = abc
BTU	British thermal unit
b	Path length in Beer's Law
BG	Base Gain
b_m	Path length of 100 meters chosen for estimation of detection limit corresponding to minimum detectable absorbance
b_r	Path length 0.160 meters used in recording calibration spectra
B/S	Beam splitter
c	Concentration in Beer's Law
c_m	Minimum detectable concentration as detection limit
COADD: 16	Coaddition of spectra, 16 spectra in this example
c_r	Concentration for calibration spectrum recorded at the lowest concentration
cm	Centimeter
cm^{-1}	Waves per centimeter or wavenumber
DA02	The model number of the Bomem interferometer
D.C.	District of Columbia
DET	Detector
EPA	Environmental Protection Agency
EV: E1	Specific aperture
FACSS	Federation of Analytical Chemistry and Spectroscopy Societies
FAX	Facsimile machine for transmitting and reproducing printed materials by telecommunication
FT1	Digital filter
FT-IR	Fourier transform infrared
FT-IRS	Fourier transform infrared system
f/4	Relative aperture or f number of 4 as ratio of focal length to diameter
GA	Georgia
GC	Gas chromatography
GC/FID/ECD	Gas chromatography with flame ionization and electron capture detection
Ge	Germanium as in KBr/Ge beam splitter
GL1	Nernst globar source of infrared radiation
HP	High pass filter
IN	Indiana

ABBREVIATIONS AND SYMBOLS (Continued)

K	Degree Kelvin
KBr	Potassium bromide as in KBr/Ge beam splitter
KS	Kansas
KSU	Kansas State University
KU	University of Kansas
KW	Kilowatt
lb	Pound
LP	Low pass filter
MC1	Mercury-cadmium-telluride No. 1 detector
MCT	Mercury-cadmium-telluride as in MCT detector
m	Meter
N	Peak to peak noise in the absorbance baseline spectrum of ambient air for a path length of 100 meters
N_2	The molecule nitrogen
OH	Ohio
PG	Positional gain
ppb	Parts per billion
P	Pressure
RES	Resolution expressed in wavenumbers, cm^{-1}
s	Second
SM	Signal post
SOURCE	Source of infrared radiation
SP	Speed
SYO	Identification of spectrum file
T	Absolute temperature
1,1,1-TCA	1,1,1-trichloroethane
VA	Virginia
VOC(s)	Volatile organic compound(s)

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SECTION 1

INTRODUCTION

Today, one of the major environmental problems is the identification of the origin and amounts of volatile organic compounds (VOCs) being actively emitted from the soil and other area sources into the atmosphere (1-7). There are many sources of VOCs, e.g., landfills (both closed and active), grain elevators (where chemical fumigants have been used), industrial sites, surface waters (lakes and lagoons), surface impoundments (both closed and active), container storage areas (drums and other containers), chemical spills (both old and recent), leaking tanks (underground, in-ground, and above ground), land treatment units, waste piles (both closed and active), water sludge deposits, air stripping plants, and indoor areas. The presence of many possible sites containing VOCs makes a rapid and reliable method for on-site analysis extremely attractive. Such a method should provide a survey of a site without the necessity of collecting many samples in canisters for later analysis at a central laboratory. An open path infrared spectrometer shows promise for this application.

A mobile system has been developed at Kansas State University (KSU) to measure volatile organic compounds (VOCs) in the atmosphere using a Fourier transform infrared (FT-IR) spectrometer (8-13). The mobile FT-IR spectrometer system was developed to do on-site measurements and analyses so that results can be obtained and reported more quickly. This technique has been tested in controlled and field locations as part of the Superfund Innovative Technology (SITE) program of the U.S. EPA.

As will be described in more detail in the Field Study Design subsection of the Materials and Methods section, 16 spectral scans will suffice to probe 64 points in a sampling grid on a site. Rather than collecting 64 individual samples in 64 canisters, at a cost of up to $1,000 and an analysis time of up to 1 hour each, it may be possible to pinpoint a few sites for sampling by canister to supplement the open-path infrared spectra. The savings in time and cost for doing the 16 spectral scans and analyzing a few sampling canisters with the mobile laboratory will be substantial compared to collection and transportation to a central laboratory and detailed analysis (by cryogenic infrared spectrometer or other methods such as gas chromatography or mass spectrometry) of 64 sampling canisters.

Our program, up to February 1, 1990, in the development of open path infrared spectrometry is described in the Results and Discussion section which consists of subsections about the laboratory calibration results and field work results. Representative spectra are discussed, and additional spectra appear in appendices.

SECTION 2

CONCLUSIONS

A mobile high resolution Fourier transform interferometer has been evaluated in the field for detection and measurement of VOCs in the atmosphere. The high resolution capability of the instrument allowed the measurement of target compounds in the presence of atmospheric water and carbon dioxide. The instrument was transported by a mobile laboratory to a hazardous waste site where measurements of the compounds present were completed in a matter of hours.

A self-contained mobile laboratory that contains the FT-IR has been equipped to travel to any site in the continental United States for rapid examination and detection of toxic atmospheric compounds. Experiments during field studies at various sites in June 1989, demonstrated its capability to measure volatiles in the parts-per-billion range.

In the course of this study, staff from EPA Region 7 have been trained to use the mobile laboratory. Laboratory calibration of the infrared interferometer has been demonstrated as applicable for field use for some compounds. Performance of field operation of the instrument has been compared with Dr. Dennis Lane's canister sampling and gas chromatography with flame ionization (Method T14 and Method 8010) at the University of Kansas (KU).

SECTION 3

RECOMMENDATIONS

During the course of this work certain recommendations for future work were recognized. A summary of these recommendations is presented below:

1) Apply this technique to the examination of a variety of new different sites, e.g., grain elevators, lagoons, chemical spills, gasoline stations, storage tanks, incinerators.

2) Evaluate instrument sensitivity with open path lengths up to 2,000 meters.

3) Design a simple, inexpensive, backpack-size instrument for in situ studies. A near infrared Hadamard transform spectrometer is one possibility to be considered here.

4) Finish field test program designed by Mr. Jody Hudson, EPA, Region 7. This program is entitled "Project Overview for Performing a Comprehensive Evaluation of a Field Portable FT-IRS Remote Sensing Instrument, January 9, 1989".

5) Expand the target list of compounds. We anticipate a target list of about 70 volatile organic solvents.

6) Complete the calibration of target compounds.

7) Install the vacuum system and the Hanst long-path cell (160 meters) in mobile laboratory. This will be applicable for sampling of small areas or in those situations where a viable open-path is unattainable. This unit can also be used to examine the contents of a canister.

8) Prof. Peter Griffith's mobile supercritical fluid gas chromatograph system would enhance the capabilities of the mobile laboratory. This system has the capability to analyze semi and non-volatile compounds without a solvent extraction.

SECTION 4

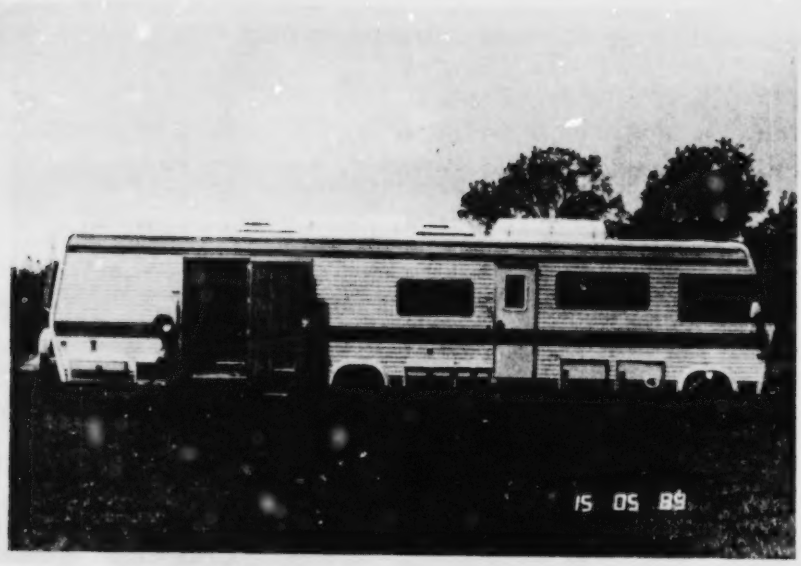
MATERIALS AND METHODS

MOBILE LABORATORY

Mobility is provided by a Journey mobile home designed to house and transport the necessary measurement instruments and the crew. A listing of some of the major features of the Journey mobile laboratory is presented in Table 1. A photograph and a schematic diagram of the general layout of the mobile laboratory is shown in Figure 1. The conversion of the mobile home to a mobile laboratory will be a continuing process. At the time of this writing, the unit is configured to house a crew of three and the following instrumentation: the FT-IR spectrometer with its collection telescope, the source of infrared radiation and its collimating telescope, appropriate computers, a weather station, a FAX machine, and a cellular telephone. The additions of a specially designed vacuum system, and a variable-path multireflection cell (White cell) to provide path lengths from 6 to 160 meters are in progress. Once the vacuum system and the variable path cell are operational, the capabilities of the mobile laboratory will include canister collection of either atmospheric gases or soil gases for analyses in the variable-path cell.

TABLE 1. SOME MAJOR FEATURES OF THE JOURNEY MOBILE LABORATORY

Journey 40′ Mobile Laboratory
-Ford 460 cu. in. Engine
-John Deere Chassis
-95 Gallon Fuel Capacity
-160 lb. Propane Capacity
-80 Gallon Water Capacity
-6.5 kw Generator
-Dual 13,500 BTU Air Conditioners
-Dual 30,000 BTU Furnaces
-Hydraulic Leveling Jacks
-10 Cubic Foot Refrigerator
-4 Burner Range w/Conventional Oven and Microwave Oven
-Three Overhead Storage Pods
-Murata FAX Machine
-Uniden CP1200 Cellular Telephone



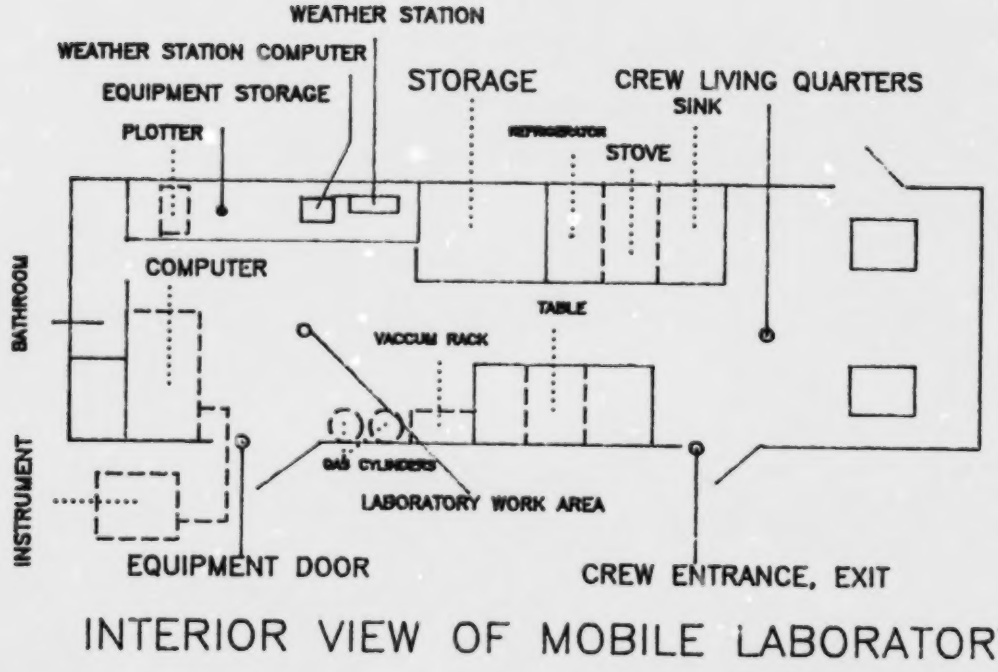


Figure 1. A photograph (A) (top) and a schematic diagram (B) (bottom) of the mobile laboratory.

FT-IR SPECTROMETER

The FT-IR spectrometer, shown in Figure 2A, is a Bomem DA02 system equipped with a KBr/Ge beam splitter, a MCT detector (liquid nitrogen cooled), a variable-height/depth tripod and a Gibralter 3 degree of motion head; the collection telescope is a 10-inch Cassegrainian.

The source of infrared radiation, shown in Figure 2B, is an air cooled and quartz shielded Nernst glower operating at 2,000 degrees Kelvin. This source is located at the focal point of a 20-inch Newtonian telescope (of 80 inch focal-length and f/4 optics with gold-coated mirrors) in order to generate a collimated beam of infrared radiation.

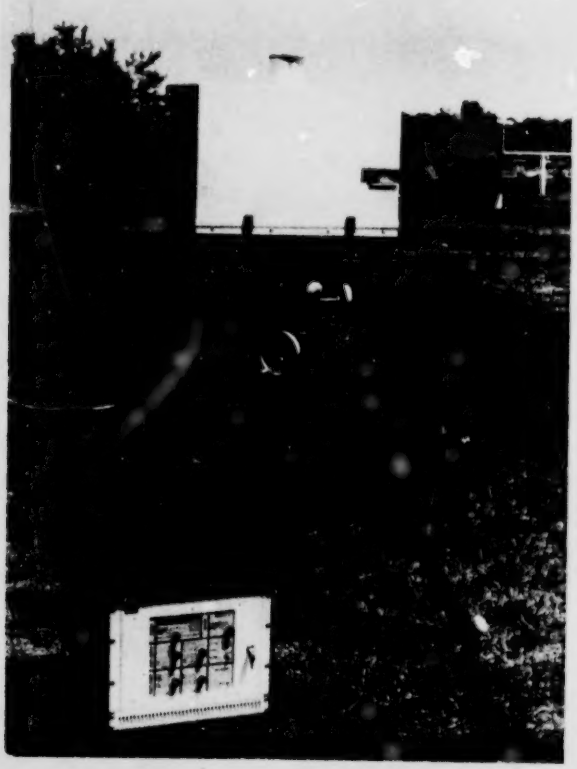
The mobile laboratory is driven to one side of the site to be surveyed, and the FT-IR spectrometer with its collection telescope is set up adjacent to the mobile laboratory. The source of infrared radiation and its collimating telescope are positioned on the opposite side of the site to be surveyed so the collimated beam of infrared radiation may be sent across the site to enter the collection telescope of the FT-IR spectrometer. An alternative arrangement is to place both the source of infrared radiation and its collimating telescope and the FT-IR spectrometer with its collection telescope adjacent to the mobile laboratory. Then a reflector is placed on the opposite side of the site so the collimated beam of infrared radiation is sent across the site to the reflector and reflected back to the collection telescope of the FT-IR spectrometer. In either arrangement, the infrared absorption spectrum of the atmosphere above the site being surveyed is used to identify any VOCs that are present in the path of the collimated beam of infrared radiation.

GC MEASUREMENTS

A limited number of confirmatory analyses were performed at Kansas University using air samples collected in Summa canisters using Method T14. The volatile compounds in these samples were measured using gas chromatography with flame ionization and electron capture detection (GC/FID/ECD).

FIELD STUDY DESIGN

The arrangement with the FT-IR spectrometer and the source on opposite sides of the site is illustrated in Figure 3 for a grid pattern of 8 spectral scans in one direction and 8 spectral scans in a perpendicular direction. Thus, a total of 16 spectral scans is necessary to spectroscopically interrogate a total of 64 intersection points. If a point source of pollutant emission is located within the grid, appropriate comparisons among the sixteen spectral scans can identify which intersection point is nearest the point source. If the emission is more uniformly distributed, comparisons among the 16 spectral scans will also identify such a condition. A crew of three can set up the instrumentation in about 30 minutes, take data for up to 30 minutes, and take down the instrumentation and move to the next scan position in an additional 30 minutes. The 16 spectral scans would then require 24 working hours and would require 2 to 3 working days. Once the site has been surveyed in this manner, individual samples at intersection points of



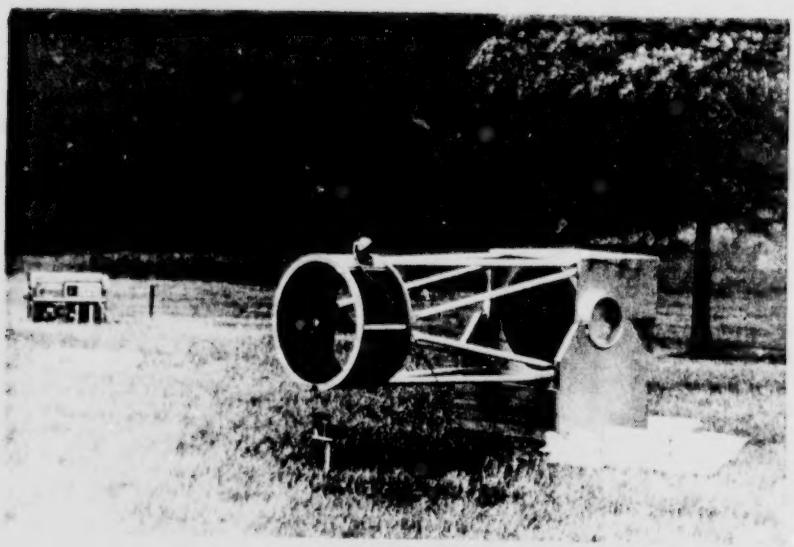


Figure 2. The FT-IR spectrometer and its collection telescope (A) (top) and the source of infrared radiation and its collimating telescope (B) (bottom).

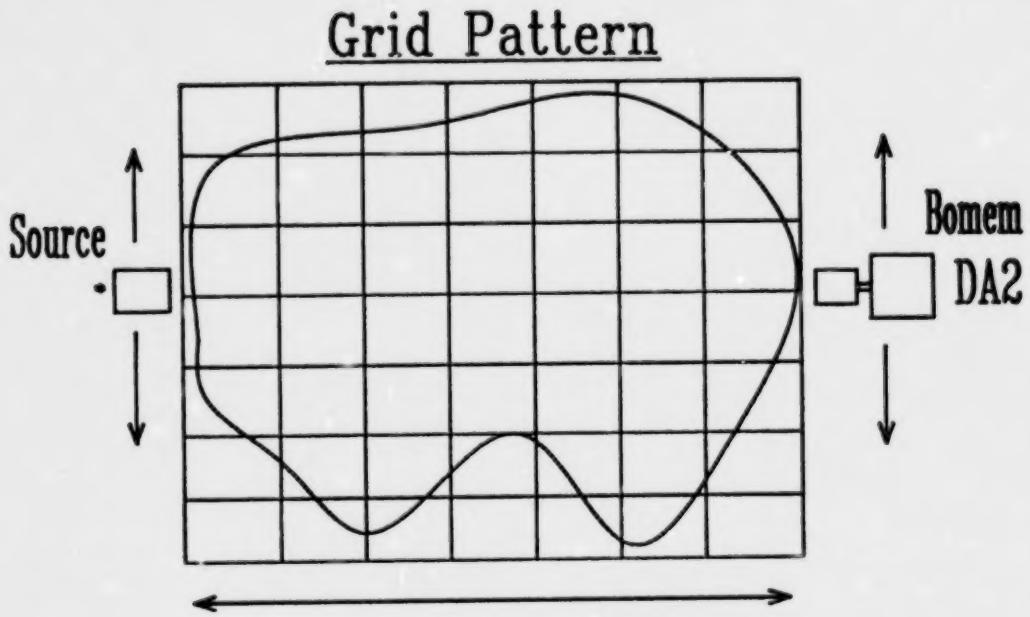


Figure 3. A possible sampling arrangement for obtaining a grid of 64 intersection points by taking 16 spectral scans.

interest may be taken for delivery to an appropriate EPA laboratory for more detailed analysis. The savings in time and money (estimated $500-1000/sample) promise to be substantial compared to taking canister samples at all 64 intersection points and returning 64 samples to an appropriate EPA laboratory for detailed analysis.

SECTION 5

RESULTS AND DISCUSSION

LABORATORY CALIBRATION RESULTS

The task of building a library of calibration spectra has begun. Two uses of the calibration spectra are: (1) to identify the VOCs that are present in the path of the collimated beam of infrared radiation between the source of infrared radiation and the FT-IR spectrometer; (2) to make estimates of the detection limits corresponding to one or more of the absorption bands in the infrared spectrum of each compound in the library. The parameters chosen for recording these calibration spectra appear in Table 2. These calibration spectra were all recorded in a fixed path cell of length 16 cm.

We are now using a variable path, multi-reflection cell (White cell). This variable path cell may be used in a normal laboratory setting for obtaining calibration spectra at a variety of path lengths if necessary or may be installed in the mobile laboratory and used for on-the-spot analysis. We currently have an air sampling canister containing accurately known concentrations of a multi-component volatile organic compound (VOC) mixture. This was supplied by the EPA Region 7 laboratory for analysis as a test of our methods. A preliminary analysis using the fixed path-cell of length 16 cm suggests that the variable path-cell will be helpful in the complete analysis of the sample supplied by the EPA Region 7 laboratory.

The calibration spectra are used in conjunction with ambient air background spectra obtained in field measurements to make estimates of

TABLE 2. PARAMETERS USED IN RECORDING CALIBRATION SPECTRA

Cell length:	16 cm
Partial Pressure:	variable-in range 0.006 - 0.28 torr
Total Pressure (with N_2):	~740 torr (nominal)
Resolution[a]:	0.1 cm^{-1} or 0.5 cm^{-1}
Number of Coadded Scans:	256
Scan Speed:	1.5 cm s^{-1}
Apodization:	Boxcar

[a]All spectra were recorded at 0.1 cm^{-1} spectral resolution and in many cases the resolution was degraded to 0.5 cm^{-1} by smoothing.

detection limits as follows. Single beam ambient air spectra taken in the field for a path-length of 100 meters are ratioed to obtain the absorbance baseline spectrum of ambient air. The minimum absorbance that would be detectable in a path-length of 100 meters is taken as 3 N. N is the peak to peak noise at the wavenumber of the absorption band in the absorbance baseline spectrum of ambient air for a path-length of 100 meters. Then use is made of Beer's Law (i.e., A = abc where A is the absorbance of the band, a is absorption coefficient in units of [(path length)(concentration)]$^{-1}$, b is path-length, and c is concentration). For a band of the minimum detectable absorbance, A_m, Beer's Law is $A_m = 3N = ab_mc_m$ with b_m = 100 meter and c_m the minimum detectable concentration in parts per billion (ppb). For the laboratory calibration spectrum, Beer's Law is $A_r = ab_rc_r$ where b_r is 0.160 meter and c_r is the lowest measured concentration in ppb. The value of c_m, the minimum detectable concentration in ppb, is obtained by taking the ratio of the two Beer's Law equations and solving for $c_m = (3N/A_r)(0.160/100)c_r = (4.8\times10^{-3}\ N/A_r)c_r$. In doing these calculations it is critical to note that concentration in molarity does not change in the gas cell for a given amount of material in the fixed volume as total pressure and/or temperature change but concentration in ppb does change. Thus, the value of c_r in molarity must be converted to ppb for the same total pressure and temperature as those for which c_m is being calculated in ppb.

Table 3 contains the minimum detection limits in a path-length of 100 meters for all compounds in the library of calibration spectra at the time of this writing, and estimated by the method described in the previous paragraph. These detection limits correspond to a concentration averaged over a path length of 100 meters at a given total pressure and temperature. Thus, the amount of material between the source of infrared radiation and the FT-IR spectrometer if uniformly distributed along the 100 meter path would be at the concentration given in ppb in Table 3. Atmospheric interferences will often raise these minimum detection limits. The applicability of Beer's Law to the absorption bands used to make the calculations in Table 3 was examined by obtaining all calibration spectra at four different concentrations and plotting the results as absorbance versus concentration.

The compromise between resolution and signal-to-noise ratio will be a matter of great significance in the field work. For bands that are broad relative to the spectral resolution chosen, in the operation of the FT-IR spectrometer, a higher resolution scan (smaller value of the resolution in cm^{-1}) will have approximately the same absorbance at the band maximum and a higher noise level causing a signal-to-noise ratio decrease and a poorer (i.e., higher) detection limit. Here the lower resolution scan is to be preferred. For the case where the band-width is comparable to the spectral resolution, chosen in the operation of the FT-IR spectrometer, a higher resolution scan (smaller value of the resolution in cm^{-1}) may yield a dramatic increase in the absorbance at the band maximum along with the higher noise level. In this case, the effect on the signal-to-noise ratio and the detection limit is not easily predictable and each case needs to be evaluated individually. The calibration spectra were recorded at 0.1 cm^{-1} resolution to give the flexibility of degrading the resolution, if desired. This degradation of the resolution is accomplished in the data processing either by smoothing the spectrum or by truncating the interferogram pricr to

TABLE 3. ESTIMATED DETECTION LIMITS (ppb) FOR SOME VOLATILE ORGANIC COMPOUNDS (VOCs) AT A PATH LENGTH OF 100 METERS USING AN APPROPRIATE ABSORPTION BAND FROM THE MID-INFRARED REGION

Compound	Wavenumber (cm^{-1})	Resolution (cm^{-1})	Detection Limit (ppb)[a]
Chlorinated hydrocarbons			
Allyl chloride	756.9	0.5	67
Carbon tetrachloride	795.2	0.5	6.3
Chlorobenzene	741.2	0.1	26
Chloroform	772.6	0.5	b
1,2-Dichloroethane	731.3	0.5	34
Methylene chloride	749.5	0.5	20
Tetrachloroethylene	916.3	0.5	19
1,1,1-Trichloroethane	726.3	0.5	8.1
Trichloroethylene	849.4	0.5	18
Aromatic hydrocarbons			
Benzene	673.9	0.1	c
Ethylbenzene	2794.0	0.5	31
Pyridine	700.3	0.1	c
Toluene	694.3	0.1	c
Alkane			
Cyclopentane	2966.0	0.5	7.2
Alcohols			
n-Butanol	2967.4	0.5	22.4
	1068.8	0.5	35
Ethanol	1066.1	0.5	31
Isopropanol	2982.7	0.5	19
	956.5	0.5	76
Methanol	1033.4	0.1	18
	1033.4	0.5	8.1
Ketones			
Acetone	1217.7	0.5	36
Methyl ethyl ketone	1174.2	0.5	40
Methyl isobutyl ketone	2965.4	0.5	18
Ester			
Ethyl acetate	1241.4	0.5	5.0
Ethers			
Diethyl ether	1142.9	0.5	9.3
1,4-Dioxane	2863.1	0.5	11
	1138.3	0.5	9.9
Tetrahydrofuran	2981.7	0.5	17
	1084.4	0.5	26

[a]These detection limits using concentration in parts per billion (ppb) are for P = 740 torr and T = 298 K.
[b]These measurements are being repeated.
[c]These bands fall in spectral regions containing sharp water vapor absorption bands and the detection limits are dependent on humidity.

transformation to the spectrum. The calibration spectra in the library contain examples of both cases and some of these examples are presented and discussed later (see Field Work Results). The situation becomes more complicated for spectral regions containing many sharp water-vapor absorption bands. Here, the higher resolution data may show the effect of these water-vapor bands more clearly and lead to better decisions about the best way to proceed. One option would be to use the higher resolution data to subtract out some of the water vapor bands and then degrade the resolution to reduce the noise. This procedure might minimize errors caused by sharp water vapor absorption bands broadened under lower resolution making unsuspected contributions to absorption bands from VOCs.

FIELD WORK RESULTS

Open path scans have been done at different controlled locations using five path lengths of 65, 100, 117, 120, and 250 meters. Initial observations at different industrial sites involved various open path-lengths from a few meters to 600 meters. The need for a variety of path lengths will be discussed later. Extensive initial work was done indoors at a path length of 65 meters along the length of the hallway on the third floor of Willard Hall at Kansas State University in Manhattan, Kansas. The work at the other four path lengths was done outdoors at Lawrence, Kansas in collaboration with the group from the Department of Civil Engineering at the University of Kansas headed by Dr. D. D. Lane. The University of Kansas group has developed a plume generator that releases a plume of VOCs of known characteristics as measured by gas chromatography. Work at 120 meters was done in February 1989. Work completed the week of May 15-19, 1989, was done at 100, 117 and 250 meters. The spectra to be discussed here are from the work completed in May and are for a 100 meter path or a 117 meter path (i.e., 385 feet).

The interferences caused by water vapor and carbon dioxide in the atmosphere are illustrated by the single beam transmission spectra in Figure 4. In Figure 4A (top) the full mid-infrared spectrum containing useful windows is shown while Figure 4B (bottom) contains an expansion of the window that appears to be most attractive for our purposes. Figure 5 illustrates the interference caused by water vapor lines and the poorer signal-to-noise ratio of field spectra for 1,1,1-trichloroethane by comparing the laboratory calibration spectrum in Figure 5A (top) with the field spectrum Figure 5B (bottom) both at 0.5 cm^{-1} resolution. A more favorable comparison occurs for methanol in Figure 6 where the laboratory calibration spectrum in Figure 6A (top) differs little from the field spectrum in Figure 6B (bottom) both at 0.5 cm^{-1} resolution. The average concentration of methanol in spectrum 6B is calculated to be 250 ppb and here an amount approximately 20 times smaller would give the minimum detectable absorbance.

The compromise between resolution and signal-to-noise ratio is illustrated for laboratory calibration spectra for benzene in Figure 7 where the absorption band is of comparable width to the spectral resolution chosen in the operation of the FT-IR spectrometer. Changing from a resolution of 0.1 cm^{-1} in Figure 7A (top) to 0.5 cm^{-1} in Figure 7B (bottom) lowers the peak absorbance by a factor close to 2 and reduces the noise by a comparable but larger factor making it somewhat subjective to choose which presentation is to

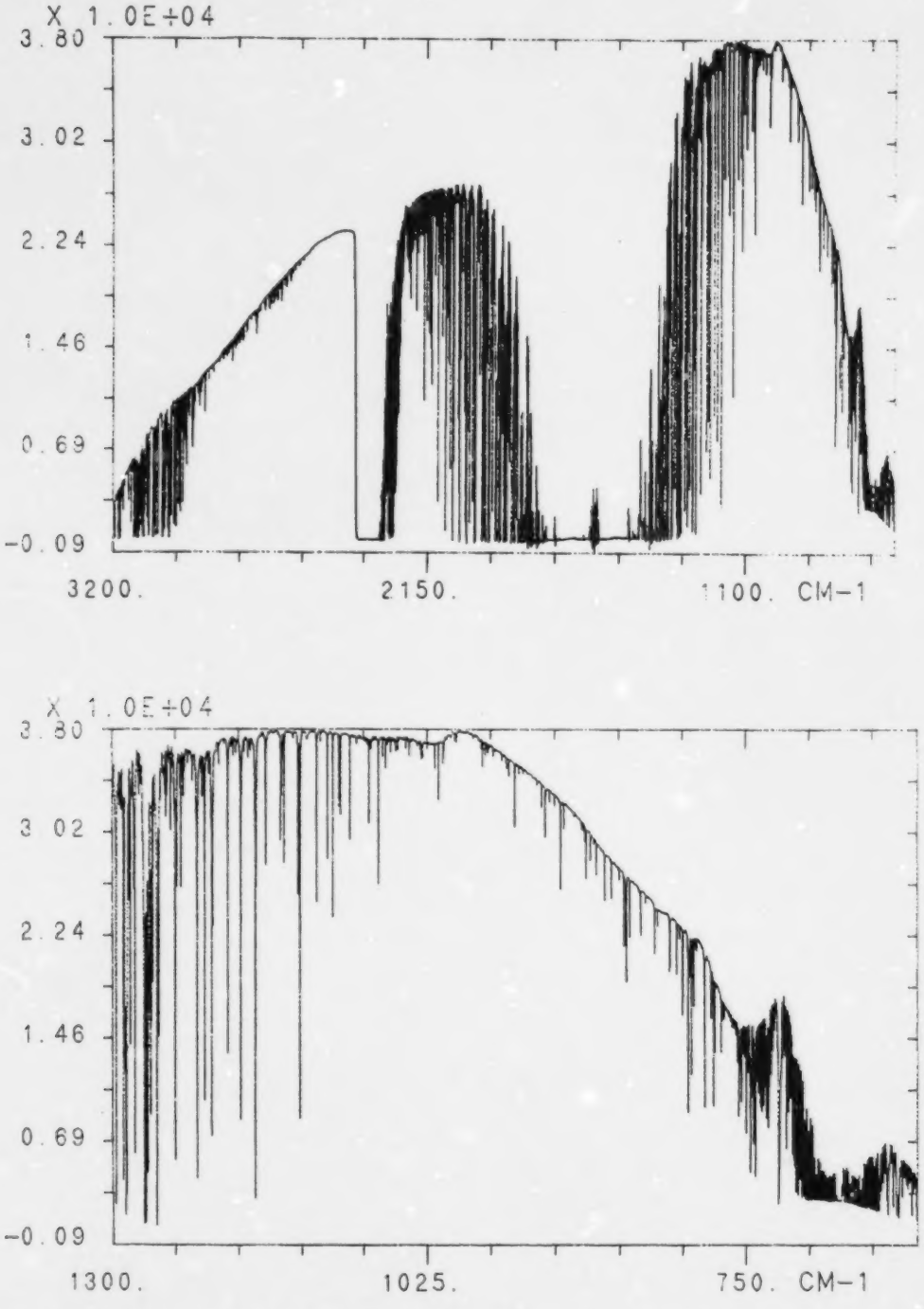


Figure 4. Single beam mid-infrared transmission spectra of 100 meters of ambient air at 0.1 cm^{-1} resolution. (A) (top) Full spectrum showing both windows. (B) (bottom) Lower frequency window expanded.

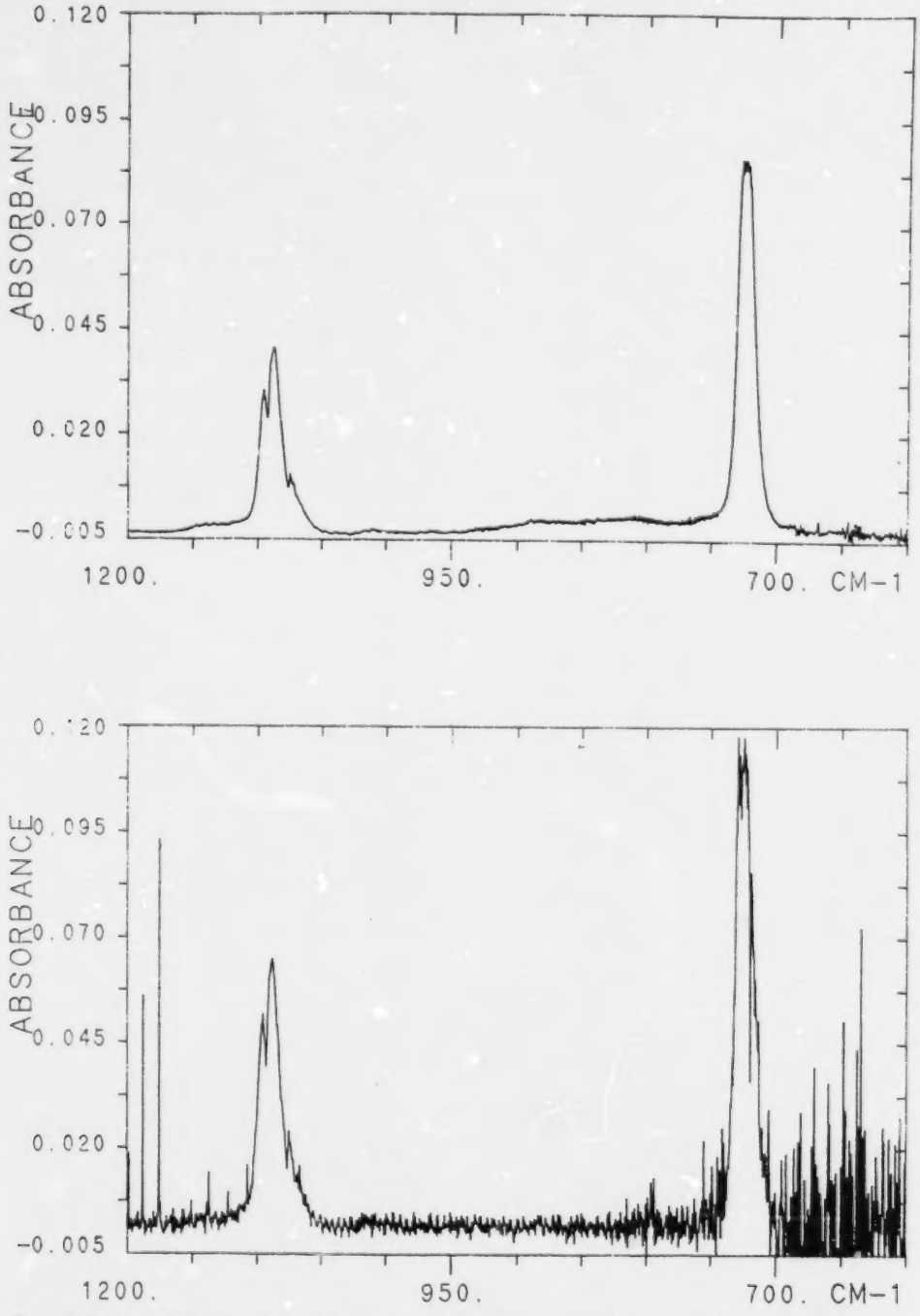


Figure 5. Mid-infrared absorbance spectra of 1,1,1-trichloroethane (1,1,1-TCA). (A) (top) Laboratory calibration spectrum in 16 cm cell at 0.5 cm^{-1} resolution. (B) (bottom) Field spectrum for 117 meters at 0.5 cm^{-1} resolution.

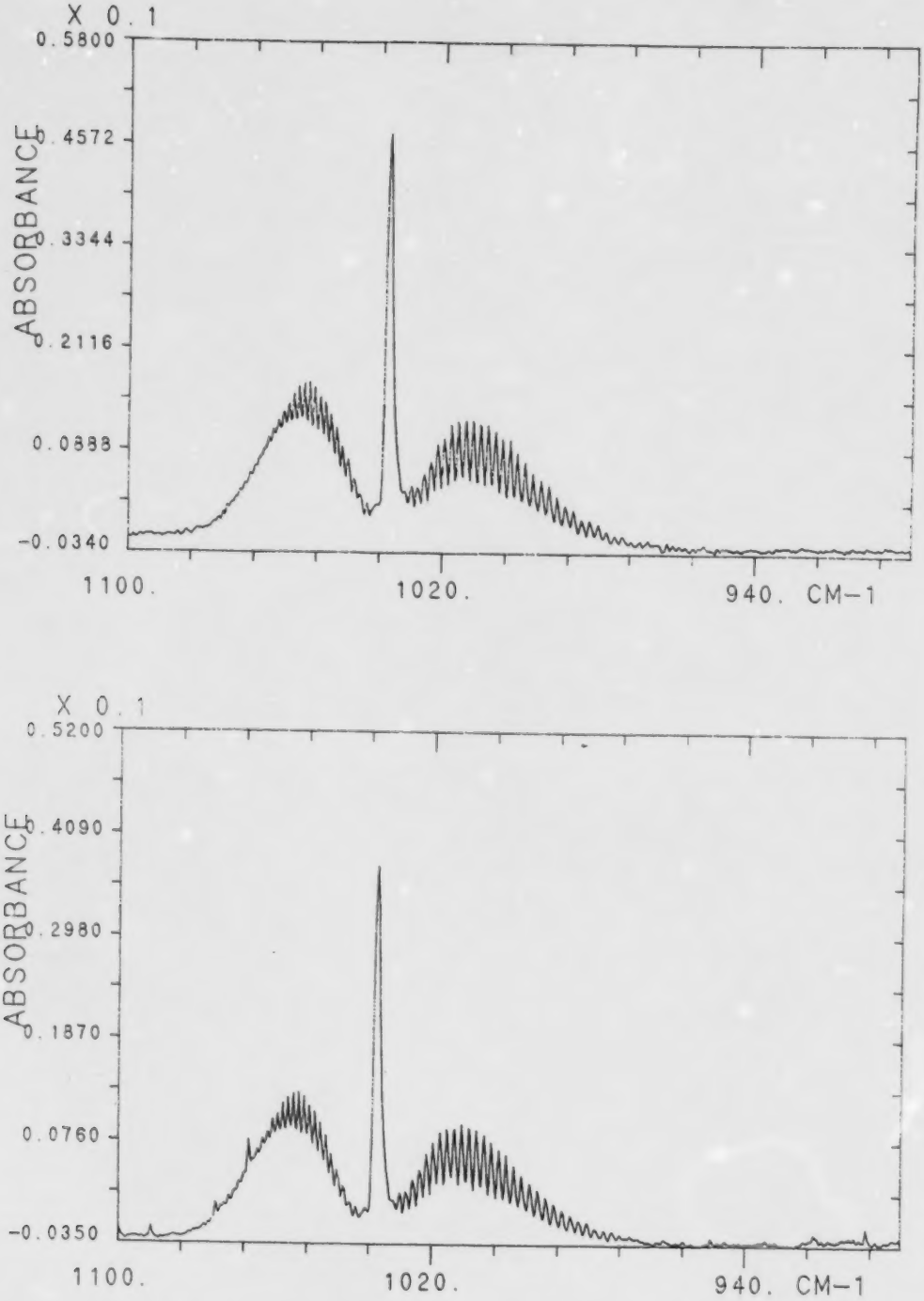


Figure 6. Mid-infrared absorbance spectra of methanol. (A) (top) Laboratory calibration spectrum in 16 cm cell at 0.5 cm^{-1} resolution. (B) (bottom) Field spectrum for 100 meters at 0.5 cm^{-1} resolution.

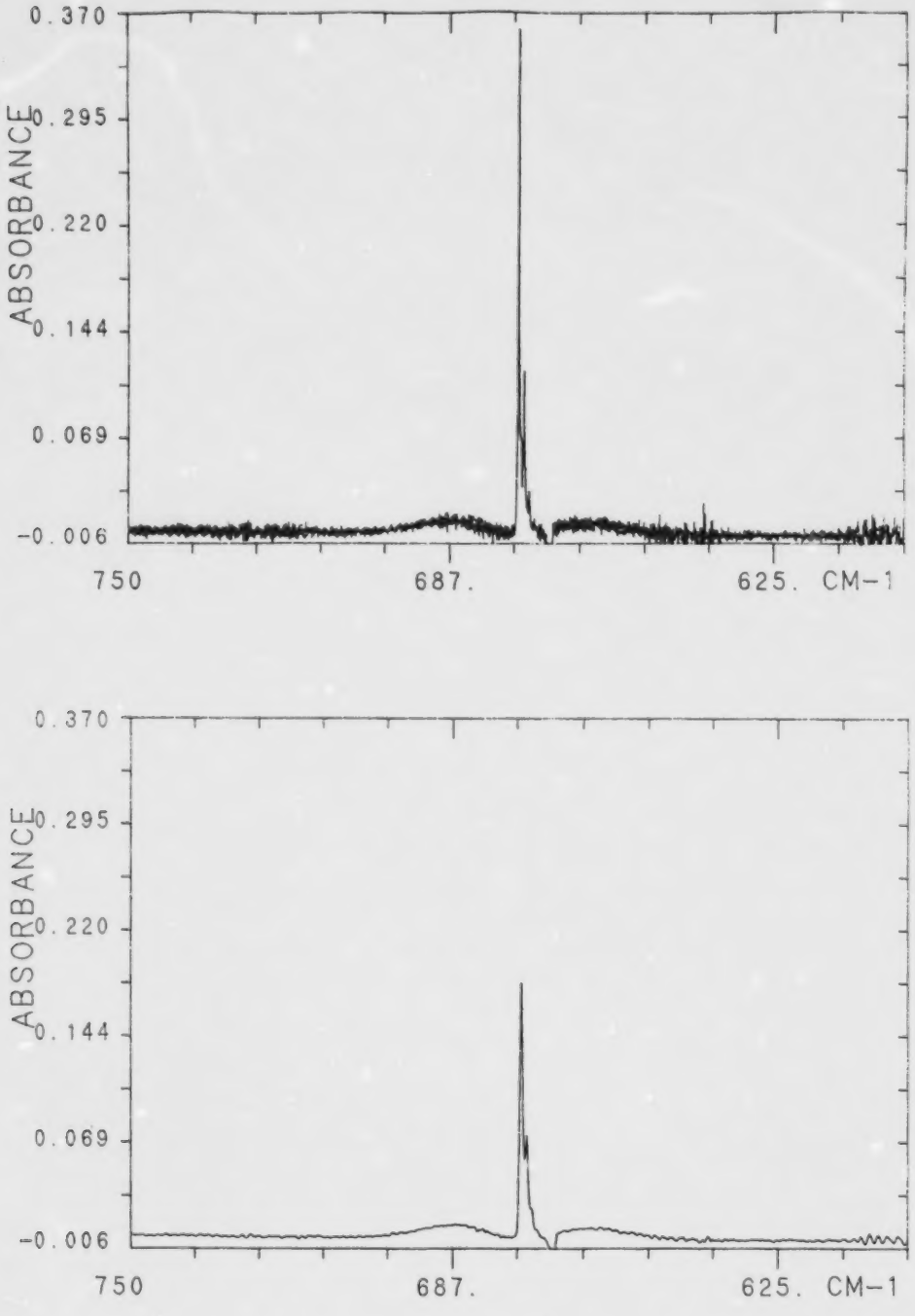


Figure 7. Mid-infrared laboratory calibration absorbance spectra of benzene. (A) (top) 16 cm cell at 0.1 cm^{-1} resolution. (B) (bottom) 16 cm cell at 0.5 cm^{-1} resolution.

be preferred for the best detection limit. The decision is complicated by the fact that the 720 to 670 cm^{-1} region contains many sharp water-vapor absorption bands and high resolution may be necessary to pick out the benzene absorption band among the absorption bands of water vapor. A definite choice is easily made for the case of the field spectra of 1,1,1-trichloroethane shown in Figure 8 where the absorption band is broad relative to the spectral resolution chosen in the operation of the FT-IR spectrometer. Changing from a resolution of 0.1 cm^{-1} in Figures 8A (top) to 0.5 cm^{-1} in Figure 8B (bottom) makes little difference in the peak absorbance and reduces the noise dramatically. Clearly, the spectrum in Figure 8B (bottom) will yield the better detection limit. Experience to date has been that the most favorable resolution to use for a given spectrum may need to be determined on-site. Our procedure to date has been to record all spectra at 0.1 cm^{-1} resolution and then degrade the resolution by reprocessing the data. Then a comparison of the different presentations as illustrated in Figures 7 and 8 is used to select the best presentation in each case.

When the choice is made to take data at this higher resolution, we then have the capability to degrade the resolution by reprocessing the data. There are two alternatives: smoothing the spectrum or truncating the interferogram and then transforming to the spectrum. Experience to date with these two alternatives is illustrated for 1,2-dichloroethane in Figure 9 where both spectra were recorded at 0.1 cm^{-1} resolution and degraded to 0.5 cm^{-1}. The spectrum in Figure 9A (top) is for smoothing the spectrum and the spectrum in Figure 9B (bottom) is for truncating the interferogram. Clearly the spectrum in Figure 9A (top) will yield the better detection limit.

The field work in February 1989 involved the release of methylene chloride as a known, and both the Kansas State University and University of Kansas groups measured an average concentration near 300 ppb. We believe that agreement between long-path FT-IR and GC/FID/ECD within 20 percent is excellent. The field work in May 1989 involved the separate release of four single materials and four multiple component samples that were unknown to KSU investigators. The following table shows the results of this testing to date.

The qualitative results presented in Table 4 are very encouraging to the authors; however, the quantitative results seem to be on the low side. This could possibly be due to error, but a greater possibility is that the infrared beam observes the atmosphere at different heights from the canisters used in this measurement. This is equivalent to stating that the canister and open-path approaches are analyzing <u>different</u> samples. In new testing at the University of Kansas this fall height factors will be addressed, as well as many other operational parameters.

The bulk of the spectral data can be reviewed in Appendix A-1. One mixture has been added to the text so it can be discussed in greater detail. Figures 10, 11, and 12 are of Mixture 3 from the KU tests. In Figure 10, we can see some fairly large interfering atmospheric absorptions. The two features most easy to identify are methanol and acetone. One immediately notices the contour of the R-Spectral Branch of methanol has changed dramatically in the region of 1055 cm^{-1}. This undoubtedly is due to the presence of n-butanol or ethanol or both. The spectrum of ethanol in

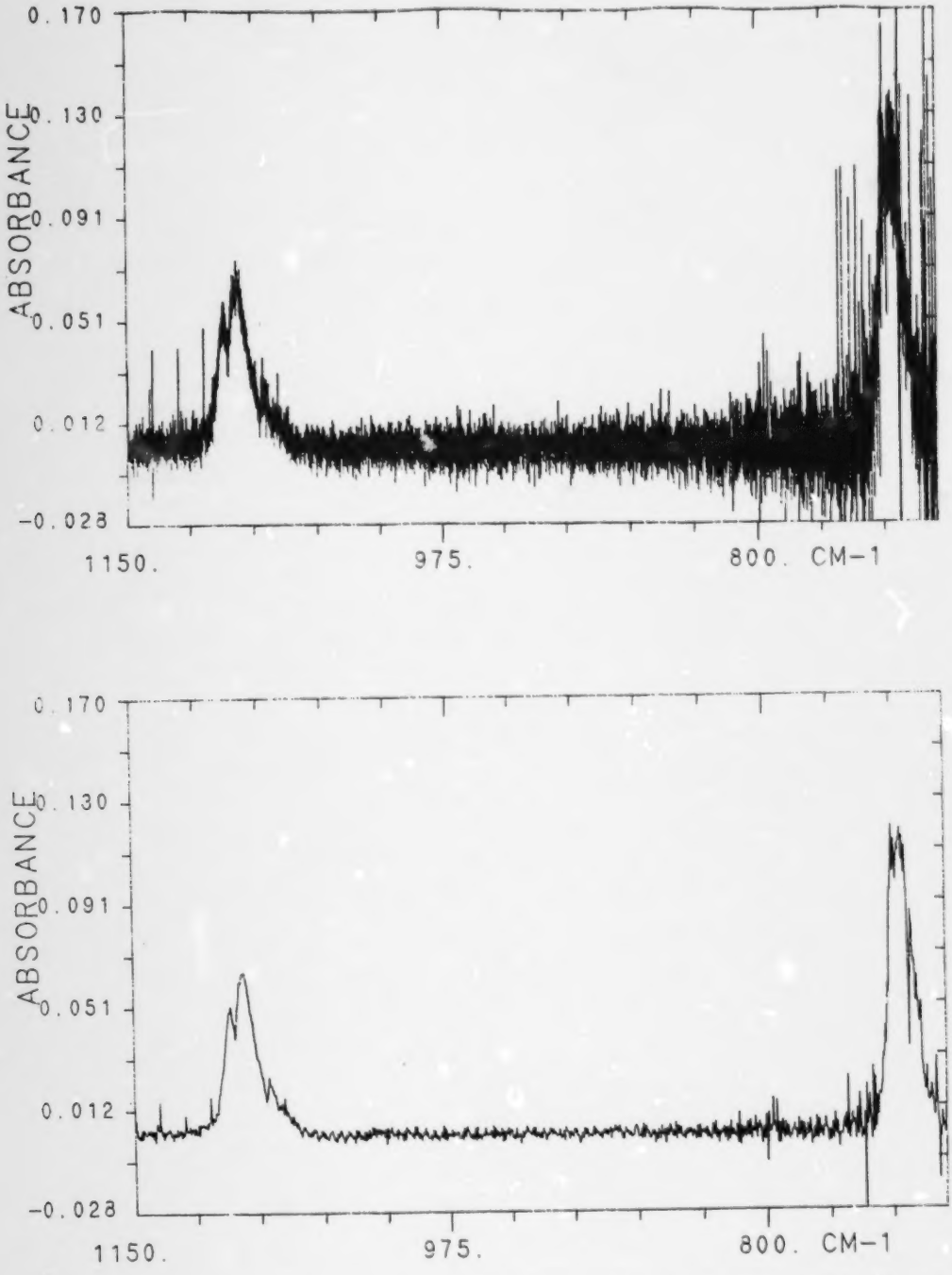


Figure 8. Mid-infrared field absorbance spectra of 1,1,1-trichloroethane (1,1,1-TCA) for 117 meters. (A) (top) 0.1 cm^{-1} resolution. (B) (bottom) 0.5 cm^{-1} resolution.

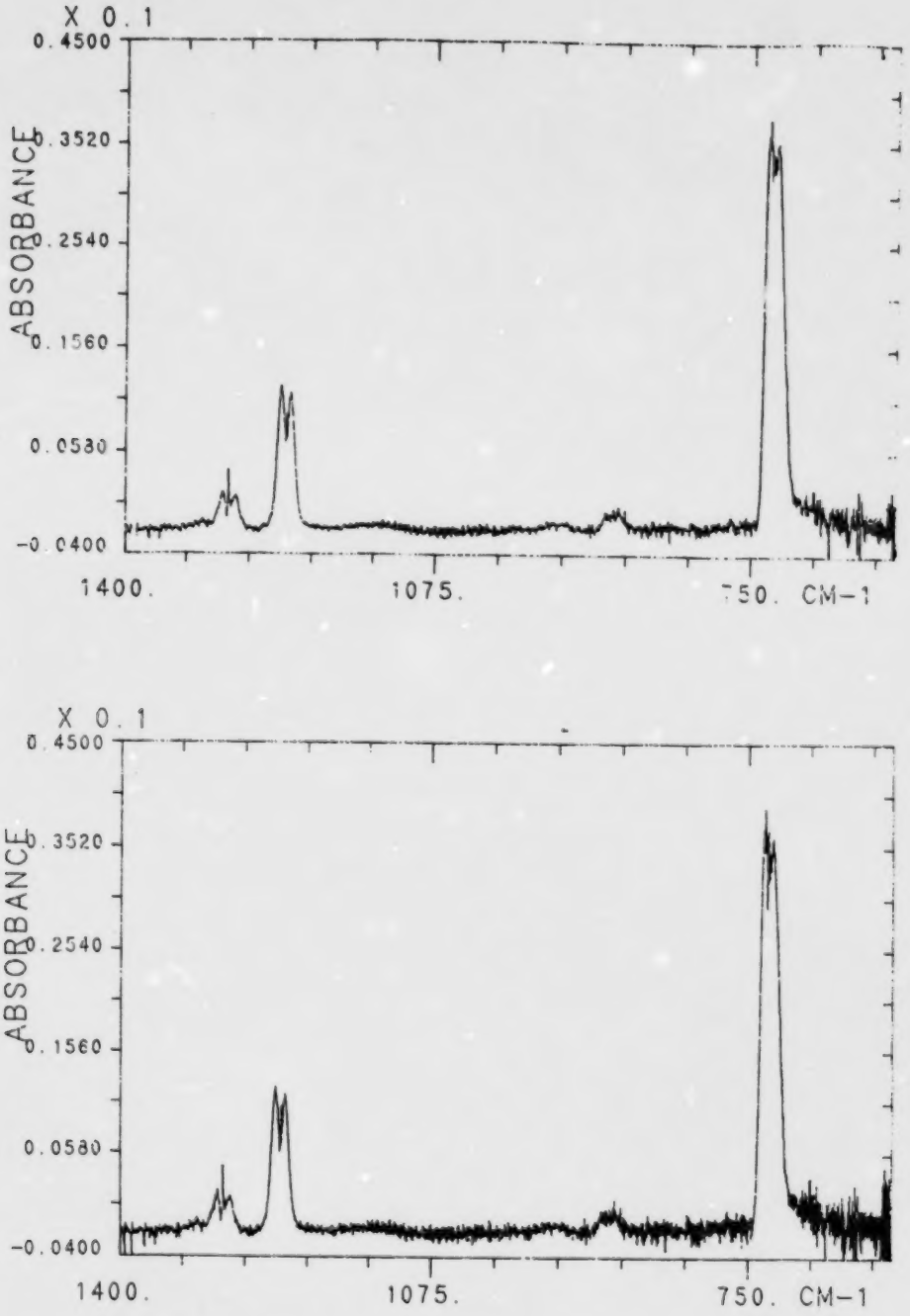


Figure 9. Mid-infrared laboratory calibration absorbance spectra of 1,2-dichloroethane in 16 cm cell. (A) (top) 0.1 cm^{-1} resolution degraded to 0.5 cm^{-1} by smoothing the spectrum. (B) (bottom) 0.1 cm^{-1} resolution degraded to 0.5 cm^{-1} by truncating the interferogram.

TABLE 4. PRELIMINARY RESULTS FROM THE TESTING AT THE UNIVERSITY OF KANSAS IN MAY 1989

Sample Label	FT-IR Assignment and Quantitation		GC/FID/ECD Measurement	
	Assignment	Average Concentration 100 m (ppb)	Actual Compound	Average Concentration 100 m (ppb)
Sample A	Acetone	44.5[a]	Acetone	b
Sample B	Methanol	148	Methanol	b
Sample C	Methylene Chloride	24.4[a]	Methylene Chloride	60
Sample D	Toluene[c]	73	Toluene[c]	110
Mixture 1	Acetone	37	Acetone	b
Mixture 1	Methylene Chloride	40.4	Methylene Chloride	75
Mixture 1	Toluene[d]	36.8	Toluene[d]	80
Mixture 2	Isopropanol	58	Isopropanol	e
Mixture 2	n-Butanol	14.4	n-Butanol	e
Mixture 2	f	--		e
Mixture 3	Acetone	97.7	Acetone	e
Mixture 3	Methanol	64	Methanol	e
Mixture 3	Ethanol	g	Ethanol	e
Mixture 3	n-Butanol[h]	g	n-Butanol	e
Mixture 4	1,1,1-TCA	18.6	1,1,1-TCA	e
Mixture 4	Methylene Chloride	42.3	Methylene Chloride	e
Mixture 4	i		Toluene	e

[a]Average concentration at 232 meters path length.
[b]KU group could not be quantitative due to the GC column in use that day.
[c]KSU group was not 100% sure of assignment of toluene. Later a viable spectral pattern for toluene was recognized and successfully used for identification.
[d]KSU group informed of toluene presence. The pattern recognization previously discovered and reported in footnote [c] was used to measure concentration.
[e]No canister samples were collected.
[f]Presence of n-pentane is suspected due to the presence of one specific band the carbon-hydrogen shielding region.
[g]Overlapping bands present; therefore, calibration has some uncertainty.
[h]Informed of its presence and were able to confirm its presence using a smaller band.
[i]Presence of toluene suspected, spectral overlap with 1,1,1-TCA.

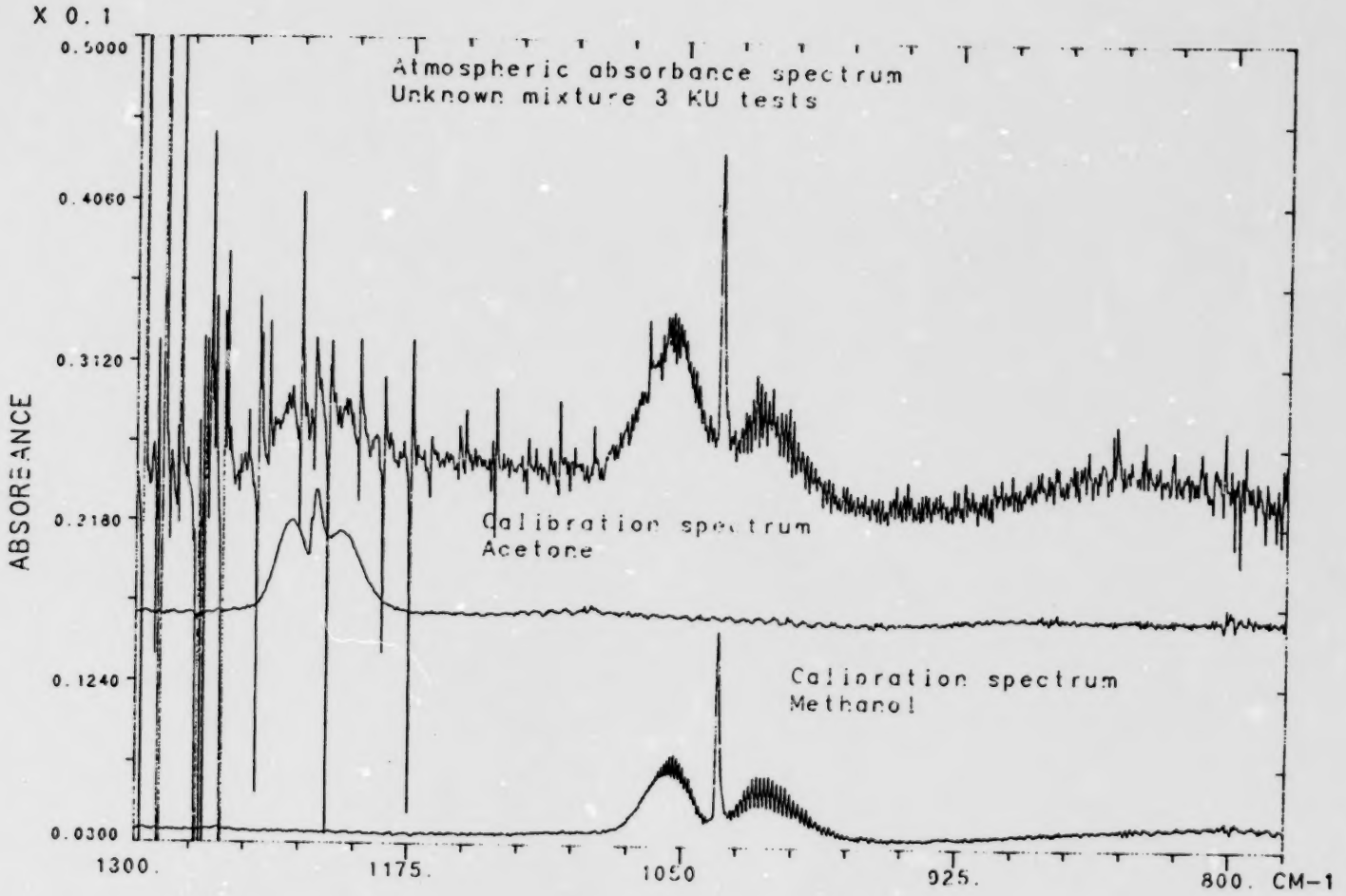


Figure 10. Mixture 3, KU tests compared against calibration spectra.

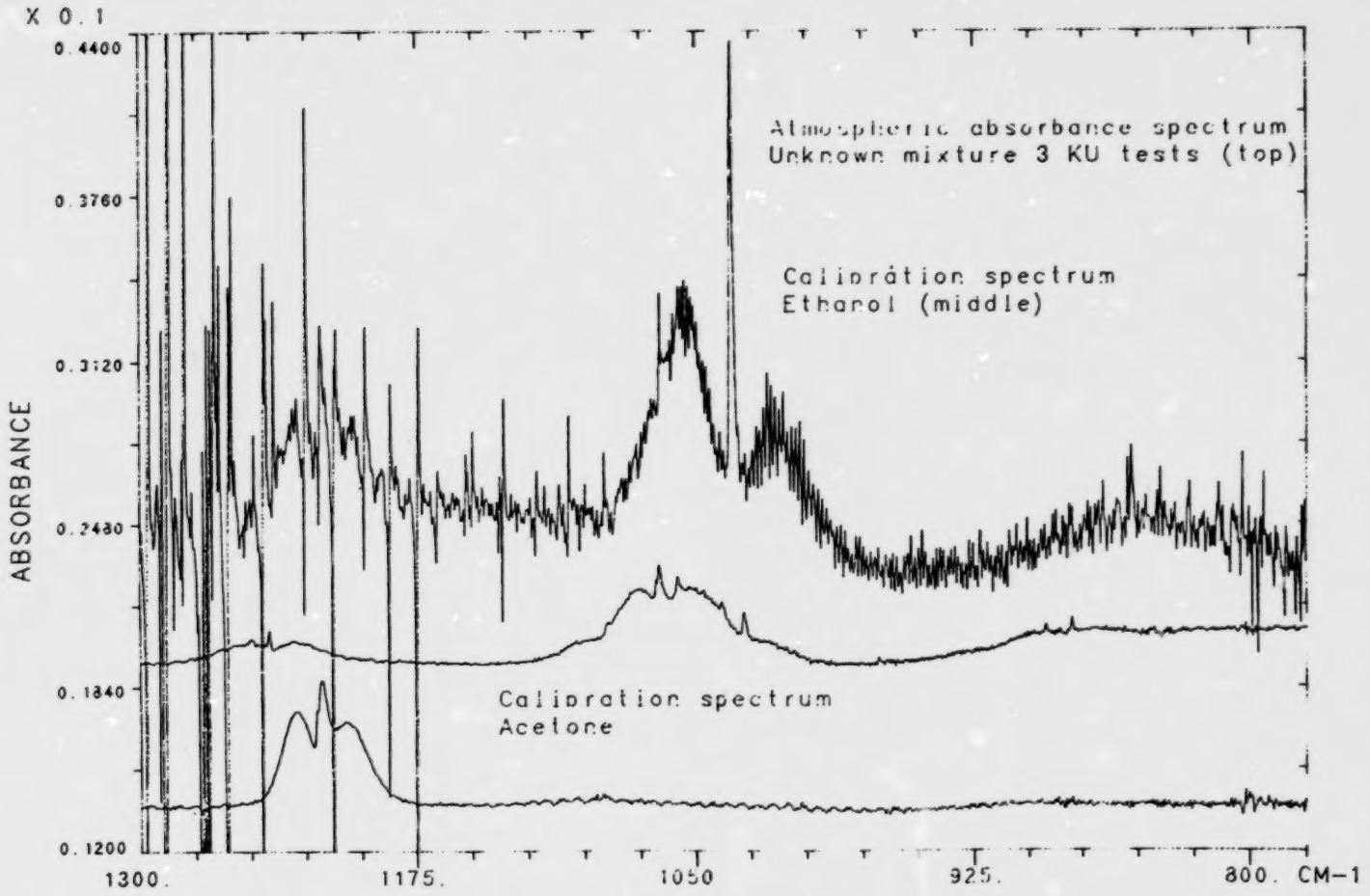


Figure 11. Mixture 3, KU tests compared against calibration spectra.

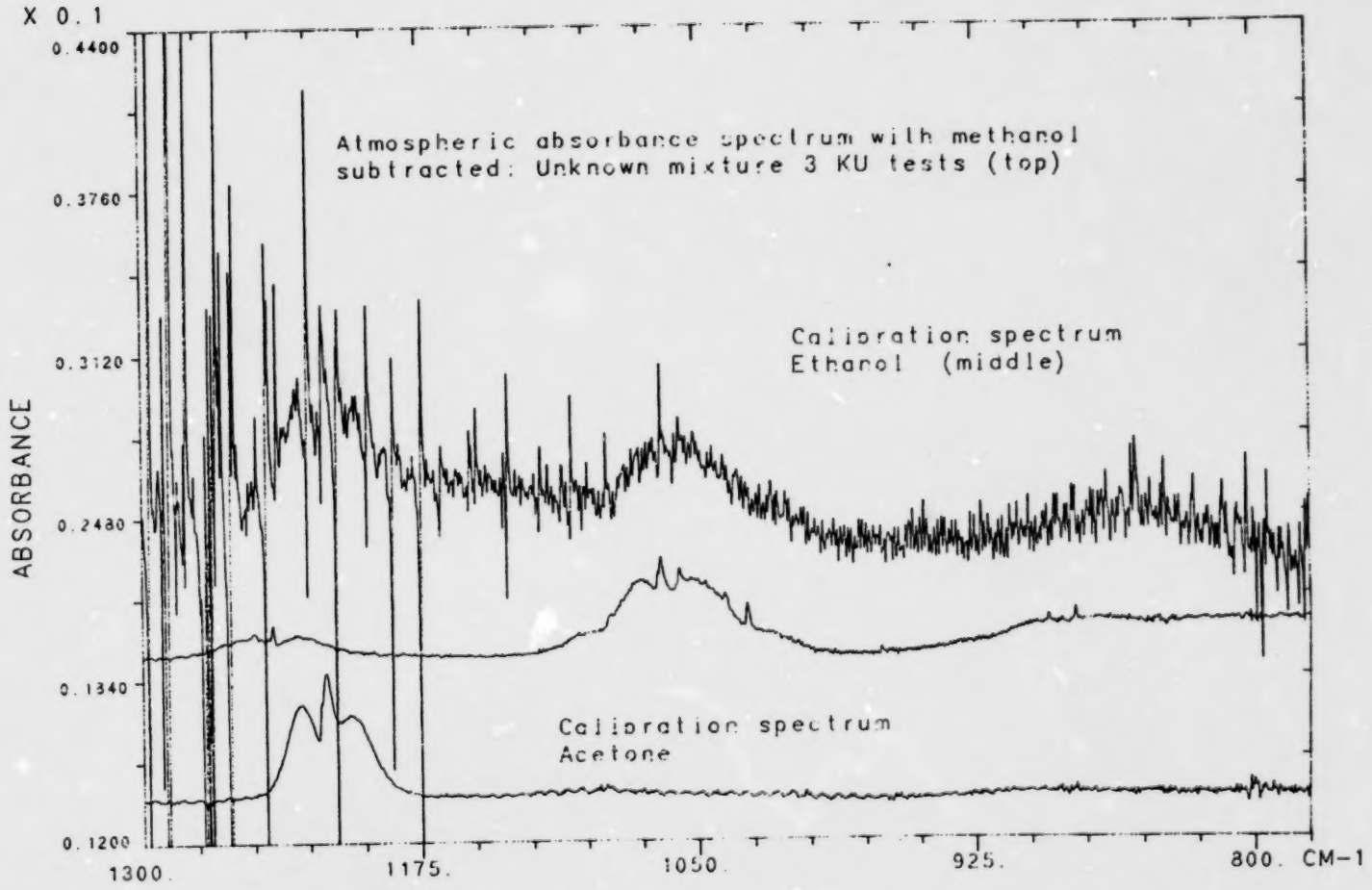


Figure 12. Mixture 3, KU tests with methanol subtracted out. Resultant spectrum compared against calibration spectra.

Figure 11 confirms this possible overlap. Figure 12 represents the resultant spectrum after the methanol has been spectrally removed. The band remaining now resembles ethanol; however, at closer observation n-butanol (not shown here) contributes to this absorbance as well.

The remainder of this section presents some results obtained at an industrial site, to which the study was allowed access so long as it was not identified. For this reason, those samples are labeled as Site A. Figure 13 contains the single beam atmospheric background spectrum upwind of Site A for a path-length of ~216 meters. A single beam atmospheric spectrum for a path-length, of ~600 meters downwind of a ditch within Site A appears in Figure 14. Although the two spectra differ in path-length by a factor of ~2.8, a comparison of Figures 13 and 14 reveals the presence of a large hydrocarbon absorption in the C-H stretching region (3,000 - 2,850 cm^{-1}) in Figure 14. This hydrocarbon absorption is illustrated in Figure 15 which is an absorbance spectrum obtained using Figure 14 as the sample and Figure 13 as the reference. Thus, the excess water-vapor spectrum for a 600 meter path ratioed against a 216 meter path is superimposed on the hydrocarbon absorption in Figure 15. An expansion of the 3,000 - 2,848 cm^{-1} region of Figure 15 appears in Figure 16 along with a laboratory calibration spectrum of isobutane. The laboratory calibration spectrum of isobutane matches rather well with extra features among the water-vapor bands which appear to be too broad to be water-vapor bands. Figure 17 reveals a change in hydrocarbon concentration at a stationary location north of an installation within site A due to a change only in time and wind direction. Here two single beam spectra for a path-length of 147 feet at this location at different times with different wind directions are ratioed to give the absorbance spectrum in Figure 17. The hydrocarbon spectrum in Figure 17 is similar to but not identical to the laboratory calibration spectrum of isobutane in Figure 16. Methane is a common constituent of the air and three lines can be recognized among the water in Figure 18 with a path-length of 147 feet on Site A. The vibration-rotation bands for both CO and N_2O are changing with time upwind of site A as shown in Figure 19 which is an absorbance spectrum obtained by ratioing the single beam spectra for a path-length of 216 meters taken at different but closely spaced time intervals. Open-path data has been acquired at additional industrial sites, but at the writing of this report these have not yet been calculated.

It seemed important to test the usefulness of this FT-IR observation on a major site as soon as possible in this program so that modifications in hardware could be made. No major difficulties were encountered in hardware. However, because of the desire to make these first early measurements, much of the calibration work and mixtures studies were left to a later date. The lack of important spectral library data and mixture analysis did slow the identification process on site. The larger target compound library which will soon be available will facilitate compound identification on site.

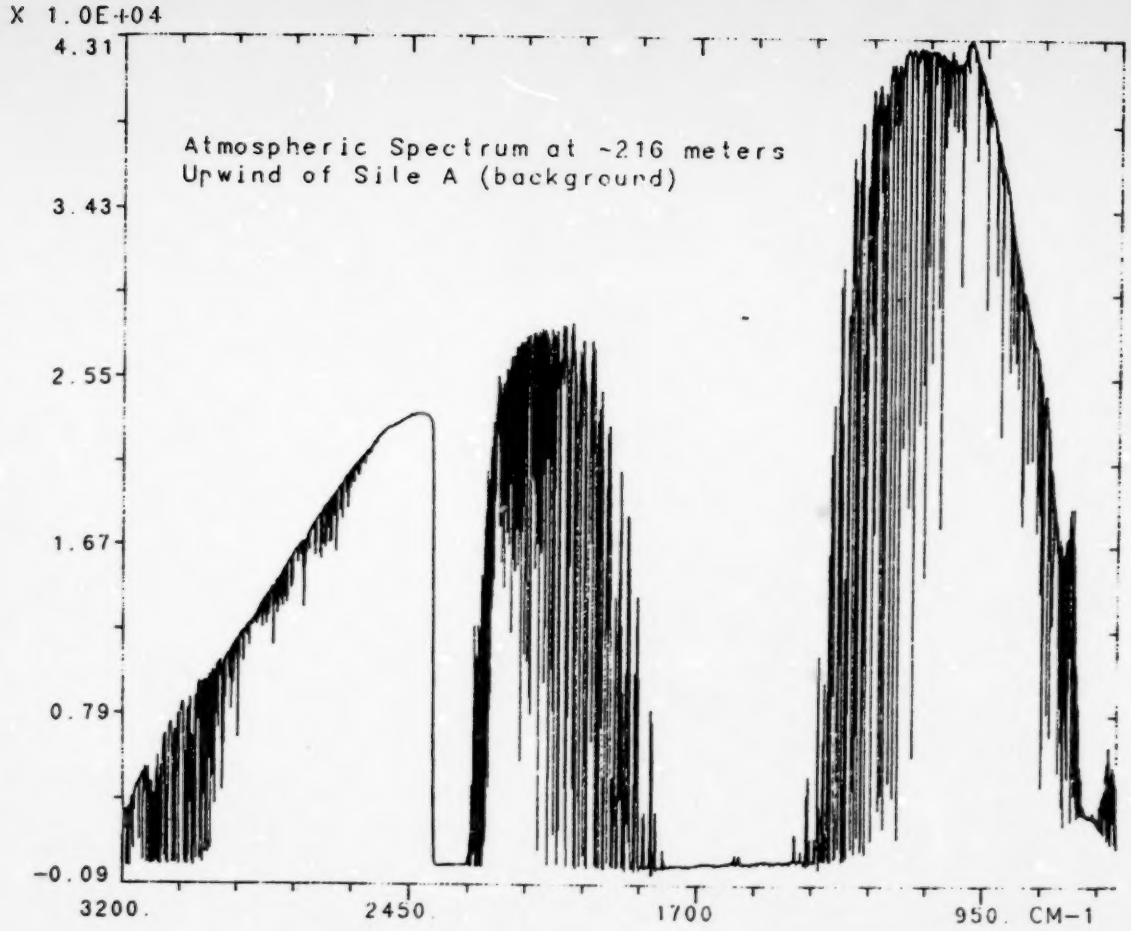


Figure 13. Single beam spectrum, ~216 meters path length, Site A.

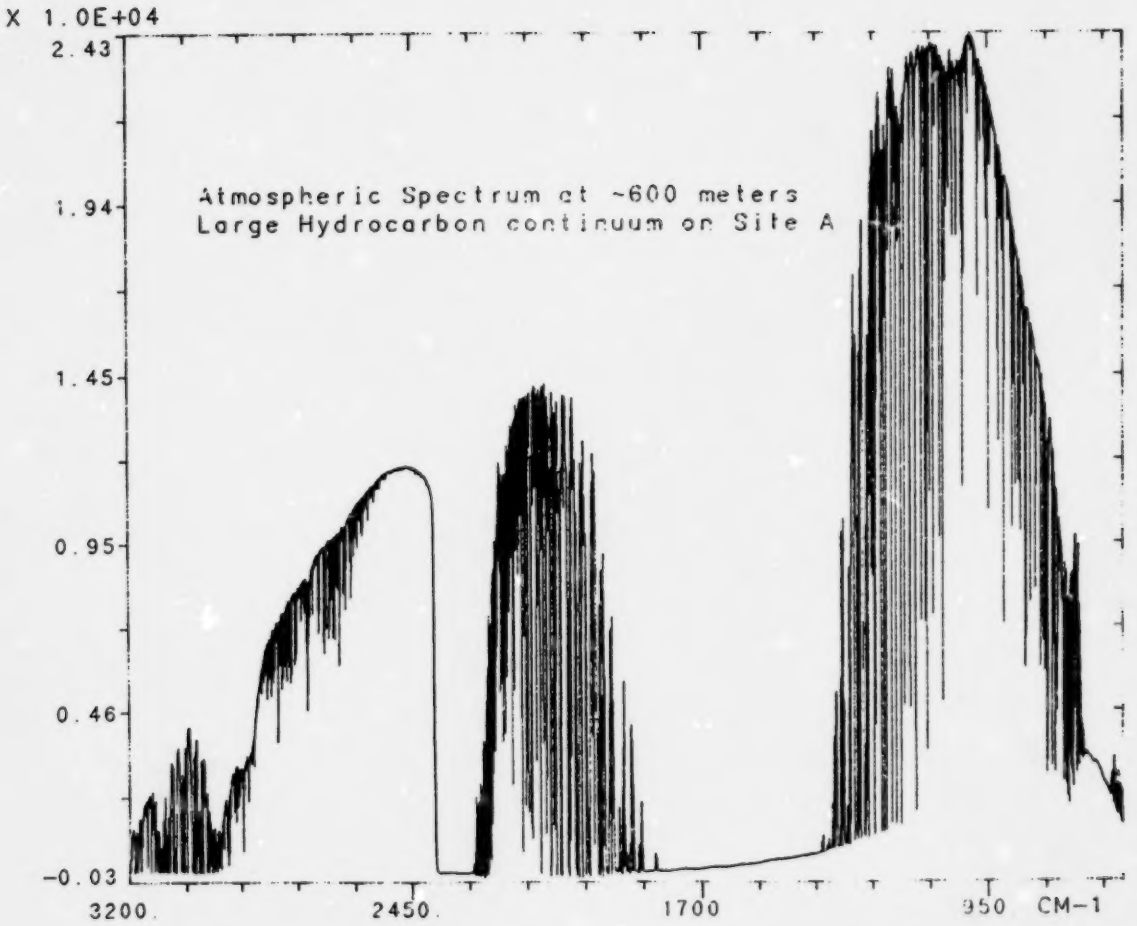


Figure 14. Single beam spectrum, ~600 meters path length, Site A, shoving strong hydrocarbon absorption.

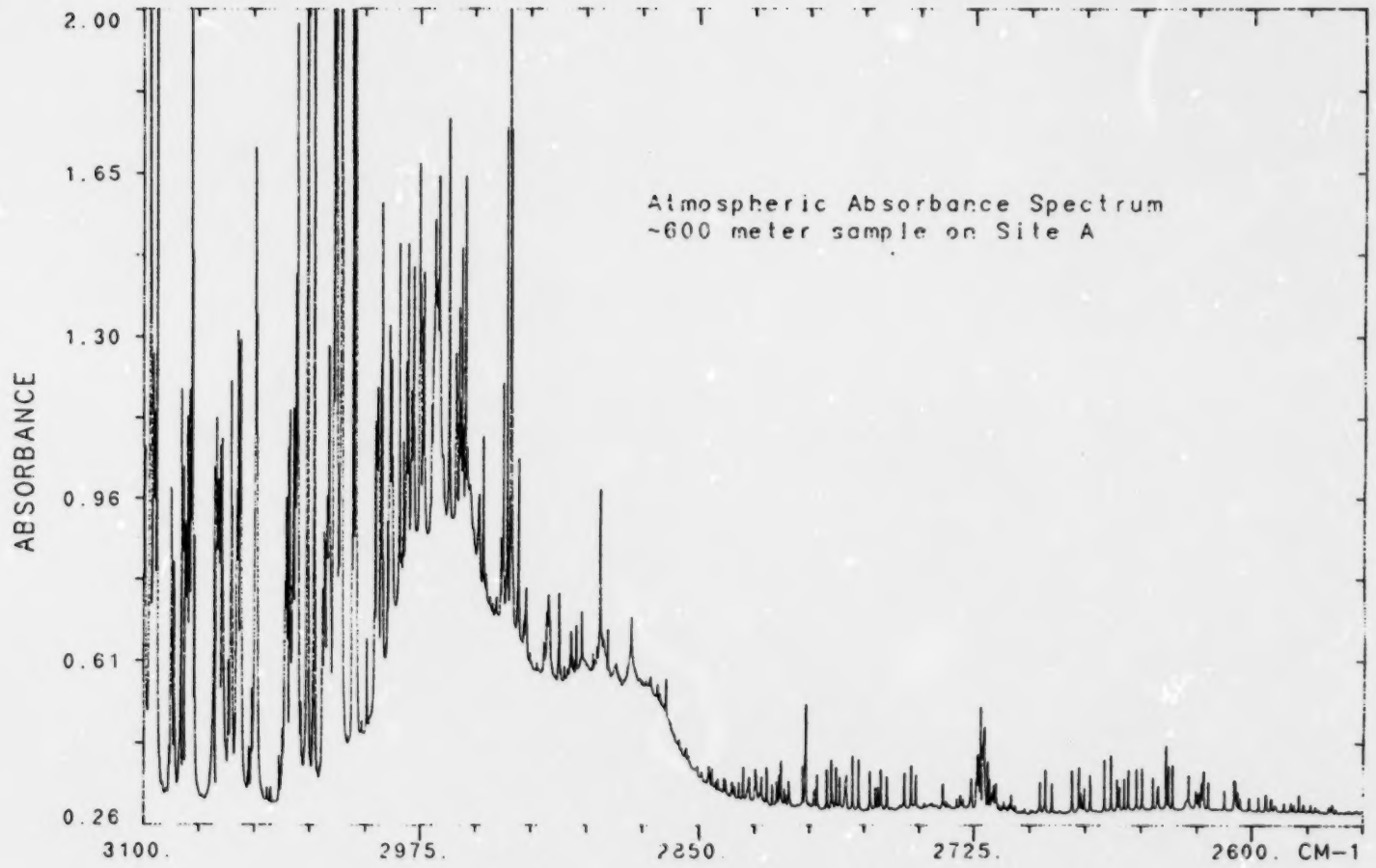


Figure 15. Figure 14 absorbance spectrum ratioed against Figure 13 spectrum, Site A.

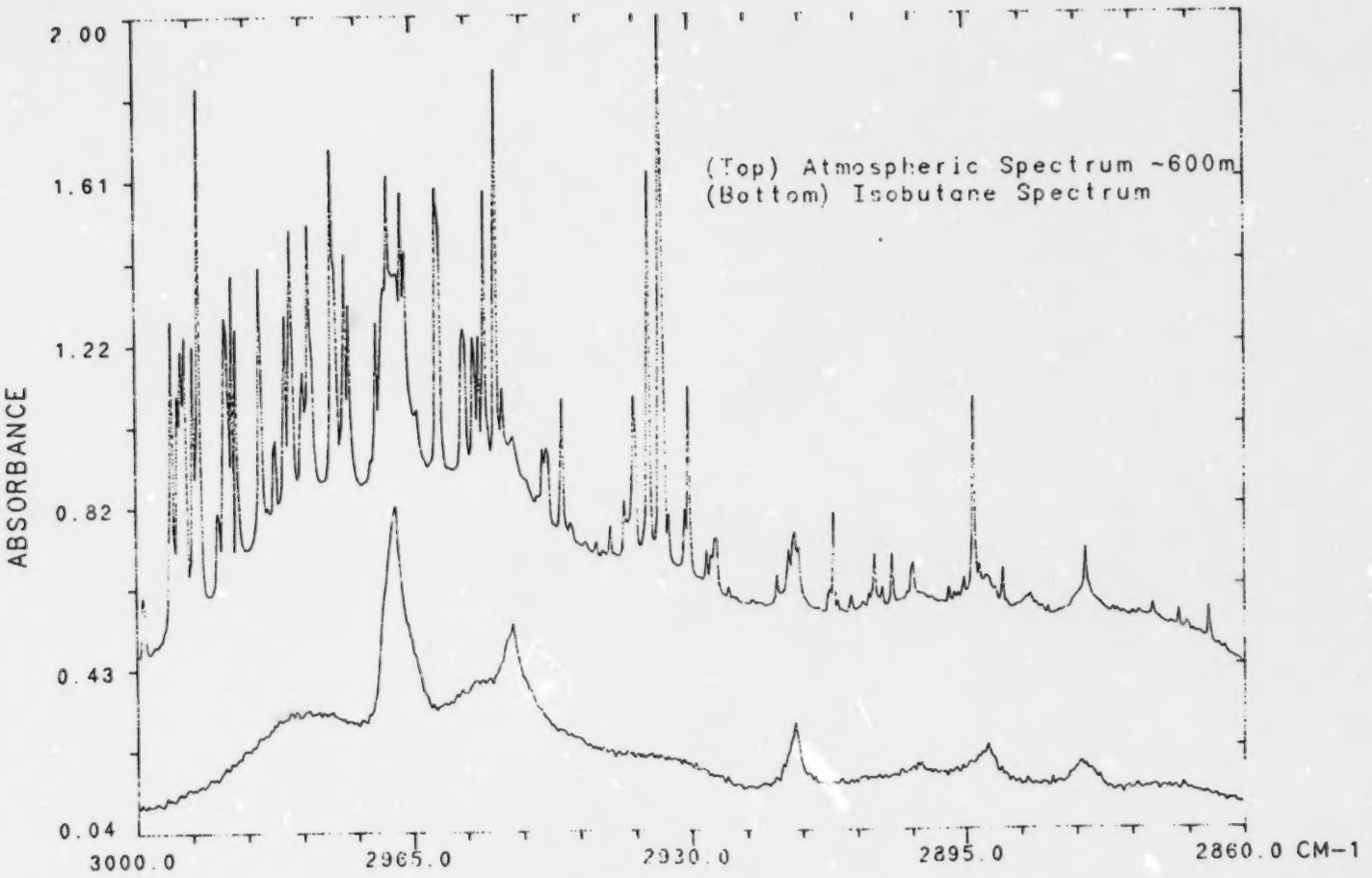


Figure 16. Absorbance spectrum, expanded Figure 15, Site A, compared against isobutane calibration spectrum.

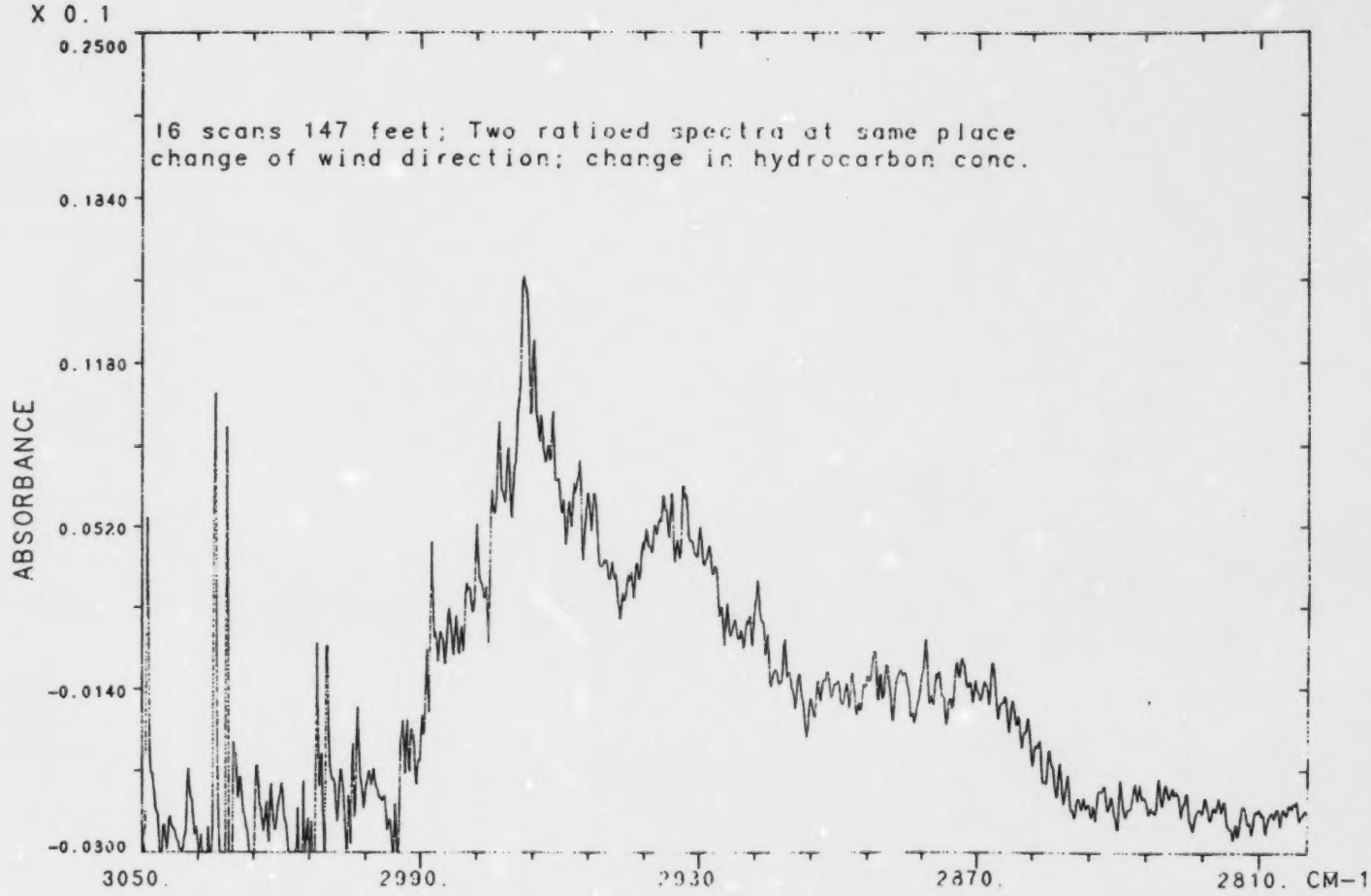


Figure 17. Absorbance spectrum, two single beams same location, different time and wind direction, Site A.

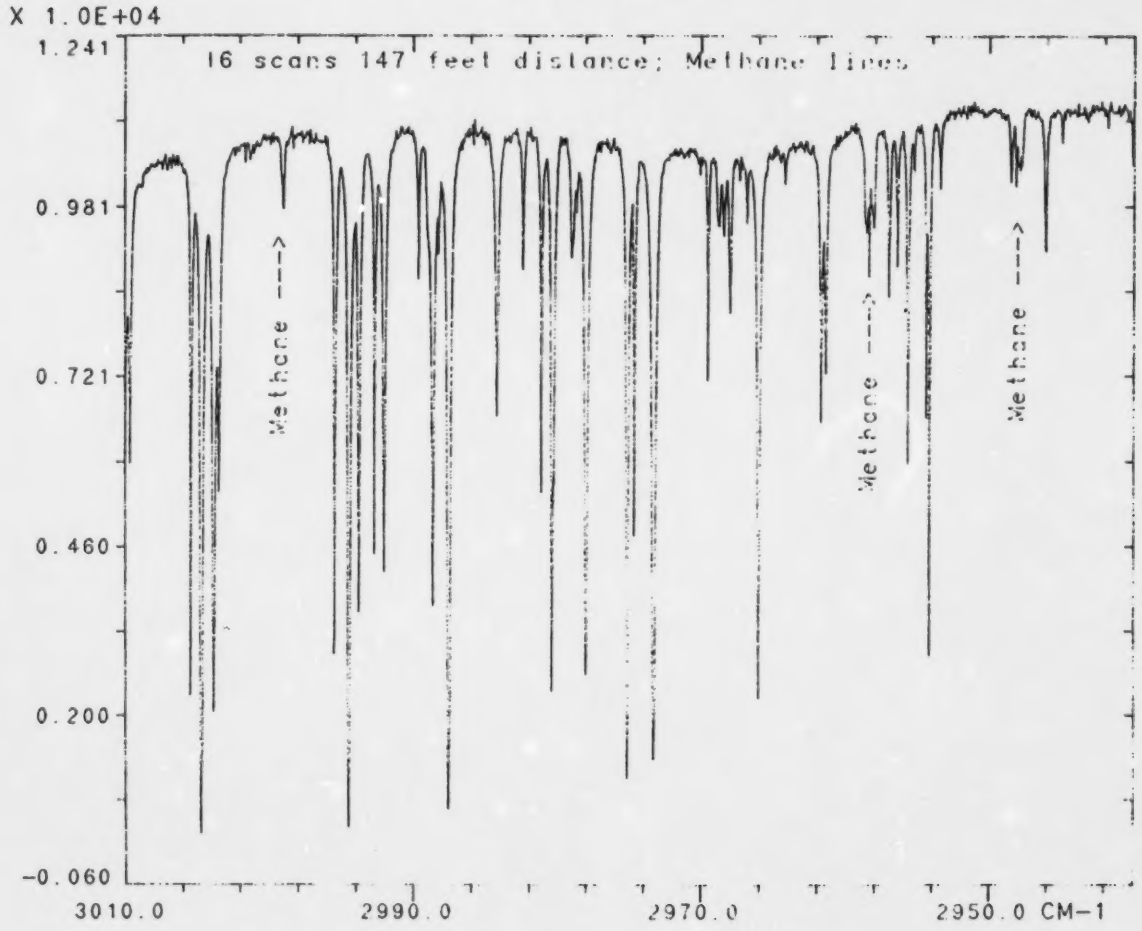


Figure 18. Single beam spectrum, showing methane absorbances between water lines, 147 feet path length, Site A.

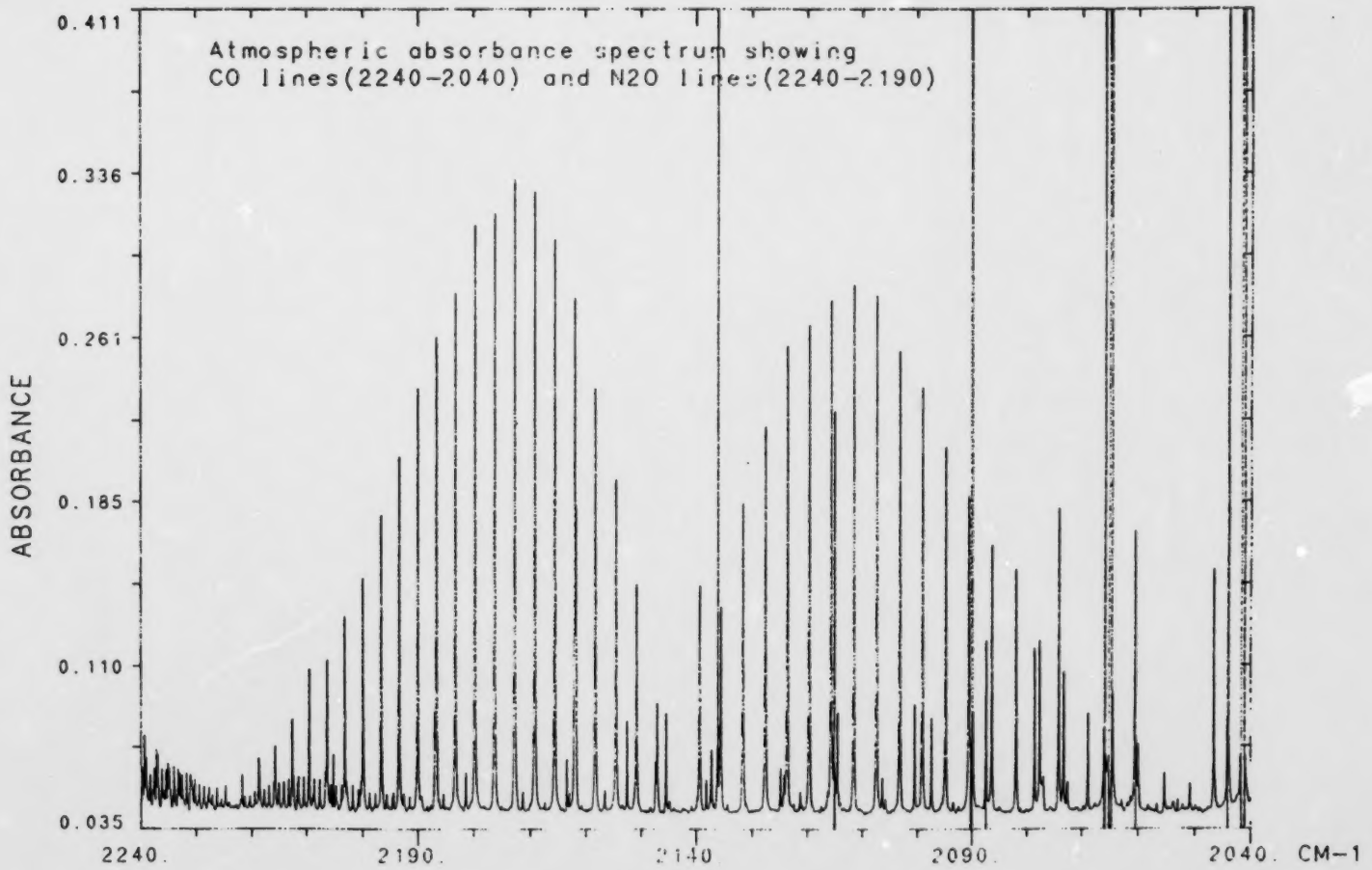


Figure 19. Absorbance spectrum, showing change in CO and N_2O concentration, ~216 meters, Site A.

SECTION 6

TECHNOLOGY TRANSFER

DEMONSTRATIONS OF THE TECHNIQUE

Four demonstrations of the mobile laboratory in its current configuration were performed at the request of Dr. Billy J. Fairless of the EPA Region 7 Laboratory in Kansas City, Kansas.

1. April 11, 1989, at the EPA Region 7 offices at 726 Minnesota Avenue in Kansas City, Kansas, for State EPA Directors by J. H. Fateley, R. M. Hammaker, and M. L. Spartz.

2. April 15, 1989, at the EPA Region 7 laboratory at 25 Funston Road in Kansas City, Kansas, for a group of Korean scientists whose visit was arranged through the office of Senator Robert Dole by J. H. Fateley, W. G. Fateley, R. M. Hammaker, and M. L. Spartz.

3. April 28, 1989, at the EPA Region 7 laboratory at 25 Funston Road in Kansas City, Kansas, for the Deputy Director of EPA by J. H. Fateley, R. M. Hammaker, and M. L. Spartz.

4. June 30, 1989, at EPA EMSL-ORD at 26 W. Martin Luther King Drive in Cincinnati, Ohio, for ESD Directors Meeting by J. H. Fateley, M. L. Spartz, and M. R. Witkowski.

ORAL AND WRITTEN PRESENTATIONS

1. "Observation and Measurements of Volatile Organic Compounds (VOC) in the Atmosphere", M. L. Spartz, R. M. Hammaker, and W. G. Fateley, Hazardous Waste Research Conference, May 25, 1988, Manhattan, Kansas (published in the conference proceedings).

2. "Remote Sensing of Volatile Organic Compounds (VOC) Using a Mobile Infrared Spectrometer System", M. L. Spartz, M. R. Witkowski, R. M. Hammaker, and W. G. Fateley, Paper 624 Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, March 6-10, 1989, Atlanta, Georgia.

3. "Design and Calibration of a Mobile Laboratory for On-Site Measurements of Volatile Organic Compounds (VOC) Using Fourier Transform Infrared Spectrometry (FT-IR)", M. L. Spartz, J. H. Fateley, M. R. Witkowski, R. M. Hammaker, and W. G. Fateley, Conference on Hazardous Waste Research, May 23-24, 1989, Kansas State University, Manhattan, Kansas (a

manuscript will be published in the conference proceedings). The mobile laboratory was displayed at this conference.

4. "A Mobile FT-IR to Measure On-Site Emissions of Volatile Organic Compounds (VOC)", M. L. Spartz, J. H. Fateley, M. R. Witkowski, R. M. Hammaker, and W. G. Fateley, Poster Paper 7th International Conference on Fourier Transform Spectroscopy, June 19-23, 1989, George Mason University, Fairfax, Virginia (a manuscript is required in addition to the abstract and poster and will be published in S.P.I.E. Proceedings). The mobile laboratory was displayed at this conference.

5. "Development of a Mobile Laboratory System for On-Site Analyses of Atmospheric Volatile Organic Compounds Using FT-IR", M. L. Spartz, M. R. Witkowski, J. H. Fateley, R. M. Hammaker, and W. G. Fateley, Department of Chemistry, Willard Hall, Kansas State University, Manhattan, Kansas 66506; R. E. Carter, M. Thomas, D. D. Lane, Department of Civil Engineering, G. A. Marotz, Department of Physics and Astronomy, University of Kansas, Lawrence, Kansas 66045; B. J. Fairless, J. Helvig, J. Hudson, U. S. Environmental Protection Agency Region 7, 25 Funston Road, Kansas City, Kansas 66115; Fifth Annual Waste Testing and Quality Assurance Symposium, July 24-28, 1989, Washington, D.C. (published in the conference proceedings).

6. "Evaluation of a Mobile FT-IR System for Rapid VOC Determination: Part 1, Preliminary Qualitative and Quantitative Calibration Results" M. L. Spartz, M. R. Witkowski, J. H. Fateley, J. M. Jarvis, J. S. White, J. V. Paukstelis, R. M. Hammaker, W. G. Fateley, R. E. Carter, M. Thomas, D. D. Lane, G. A. Marotz, B. J. Fairless, T. Holloway, J. L. Hudson and D. F. Gurka. American Environmental Laboratory. July 1989, 15-30.

7. "Field Monitoring of Air Toxics by Open-Path Fourier Transform Infrared Spectrometry." D. F. Gurka, B. J. Fairless, J. Hudson, H. Kimball, J. Helvig, J. Arello, T. Holloway, W. G. Fateley, R. M. Hammaker, M. L. Spartz, M. R. Witkowski, J. Fateley, D. D. Lane, R. Carter, M. Thomas and G. A. Marotz. Anal. Chem. 1990, 62, 0000.

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9. M. L. Spartz, J. H. Fateley, M. R. Witkowski, R. M. Hammaker, W. G. Fateley. Design and Calibration of a Mobile Laboratory for On-Site Measurements of Volatile Organic Compounds (VOC) Using Fourier Transform Infrared Spectrometry (FT-IR). In: Proceedings of the Conference on Hazardous Waste Research, May 23-24, 1989, Kansas State University, Manhattan, Kansas.

10. M. L. Spartz, J. H. Fateley, M. R. Witkowski, R. M. Hammaker, W. G. Fateley. A Mobile FT-IR to Measure On-Site Emissions of Volatile Organic Compounds (VOC). Poster Paper 7th International Conference on Fourier Transform Spectroscopy, June 19-23, 1989, George Mason University, Fairfax, Virginia (a manuscript is in S.P.I.E. Proceedings).

11. M. L. Spartz, M. R. Witkowski, J. H. Fateley, R. M. Hammaker, and W. G. Fateley, Department of Chemistry, Willard Hall, Kansas State University, Manhattan, Kansas 66506; R. E. Carter, M. Thomas, and D. D. Lane,

Department of Civil Engineering, G. A. Marotz, Department of Physics and Astronomy, University of Kansas, Lawrence, Kansas 66045; B. J. Fairless, J. Helvig, and J. Hudson, U.S. Environmental Protection Agency Region 7, 25 Funston Road, Kansas City, Kansas 66115. Development of a Mobile Laboratory System for On-Site Analyses of Atmospheric Volatile Organic Compounds Using FT-IR. In: Proceedings of the Fifth Annual Waste Testing and Quality Assurance Symposium, July 24-28, 1989, Washington, D.C.

12. "Evaluation of a Mobile FT-IR System for Rapid VOC Determination: Part 1, Preliminary Qualitative and Quantitative Calibration Results" M. L. Spartz, M. R. Witkowski, J. H. Fateley, J. M. Jarvis, J. S. White, J. V. Paukstelis, R. M. Hammaker, W. G. Fateley, R. E. Carter, M. Thomas, D. D. Lane, G. A. Marotz, B. J. Fairless, T. Holloway, J. L. Hudson and D. F. Gurka. American Environmental Laboratory. July 1989, 15-30.

13. "Field Monitoring of Air Toxics by Open-Path Fourier Transform Infrared Spectrometry." D. F. Gurka, B. J. Fairless, J. Hudson, H. Kimball, J. Helvig, J. Arello, T. Holloway, W. G. Fateley, R. M. Hammaker, M. L. Spartz, M. R. Witkowski, J. Fateley, D. D. Lane, R. Carter, M. Thomas and G. A. Marotz. Anal. Chem. 1990, 62, 0000.

APPENDIX A

SPECTRA FROM FIELD WORK AT LAWRENCE, KS

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SINGLE COMPONENT UNKNOWN FROM UNIVERSITY OF KANSAS TESTS

The four single component samples were analyzed and were found to be, in order: (A) acetone, (B) methanol, (C) methylene chloride, and (D) toluene. The concentrations were then calculated approximately and placed in Table 4. All but toluene (Sample D) provided firm results. After the analysis was confirmed by Ray E. Carter (KU) the concentration was calculated.

ANALYSIS OF UNKNOWN MIXTURE 1

There were three compounds in Mixture 1. Two of these compounds (acetone and methylene chloride) were identified by observations of the base line pattern. The third compound (toluene) was also present in this mixture. Once this was known, the presence of toluene was confirmed. See Figure A-7 where toluene, in the spectrum, can be recognized. This recognition was used in other mixtures which contained toluene.

ANALYSIS OF UNKNOWN MIXTURE 2

There were three compounds present in Mixture 2. In Figure A-8 one sees three compounds that could match the atmospheric spectrum to some extent, the isopropanol was easily recognized from the contour of the baseline. After successfully subtracting out the isopropanol, we can see the resultant subtracted spectrum in Figure A-9. It is evident that the n-butanol appears to best match the resulting spectrum. The possibility of ethanol present was not disregarded. However, it was later confirmed not to be in the mixture. The third compound was reported to be n-pentane. The ability to get a confident match and identification of n-pentane was seriously hampered by the fact that the isopropanol and n-butanol both have strong absorbances in the CH region in the same region as n-pentane.

ANALYSIS OF UNKNOWN MIXTURE 3

See the Field Work Results subsection for a discussion of this mixture.

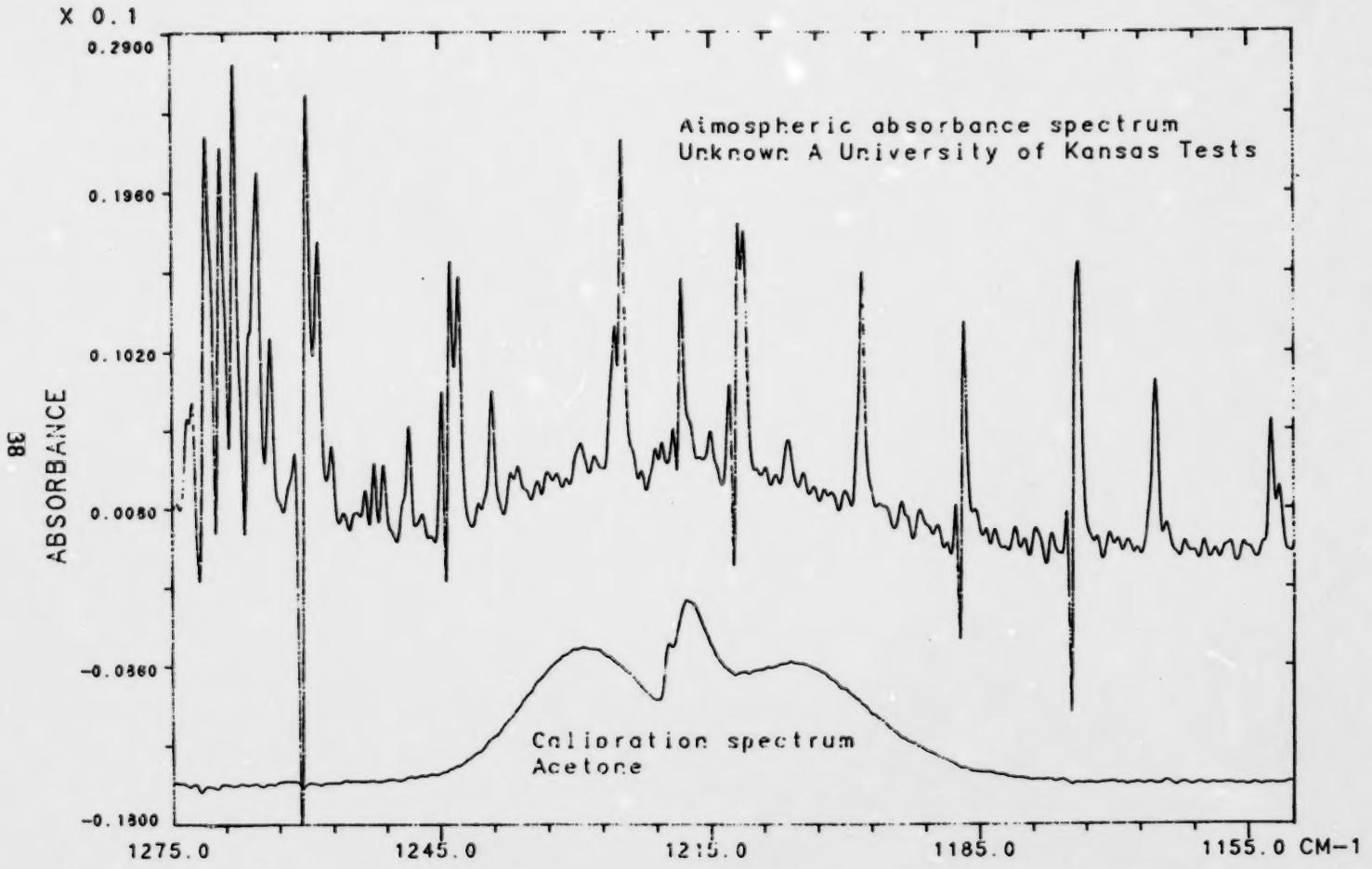

Figure A-1. Unknown Sample A (Acetone). Kansas University tests for EPA testing 5-16-89, 760 feet source 0.1 cm^{-1} res. unknown A.

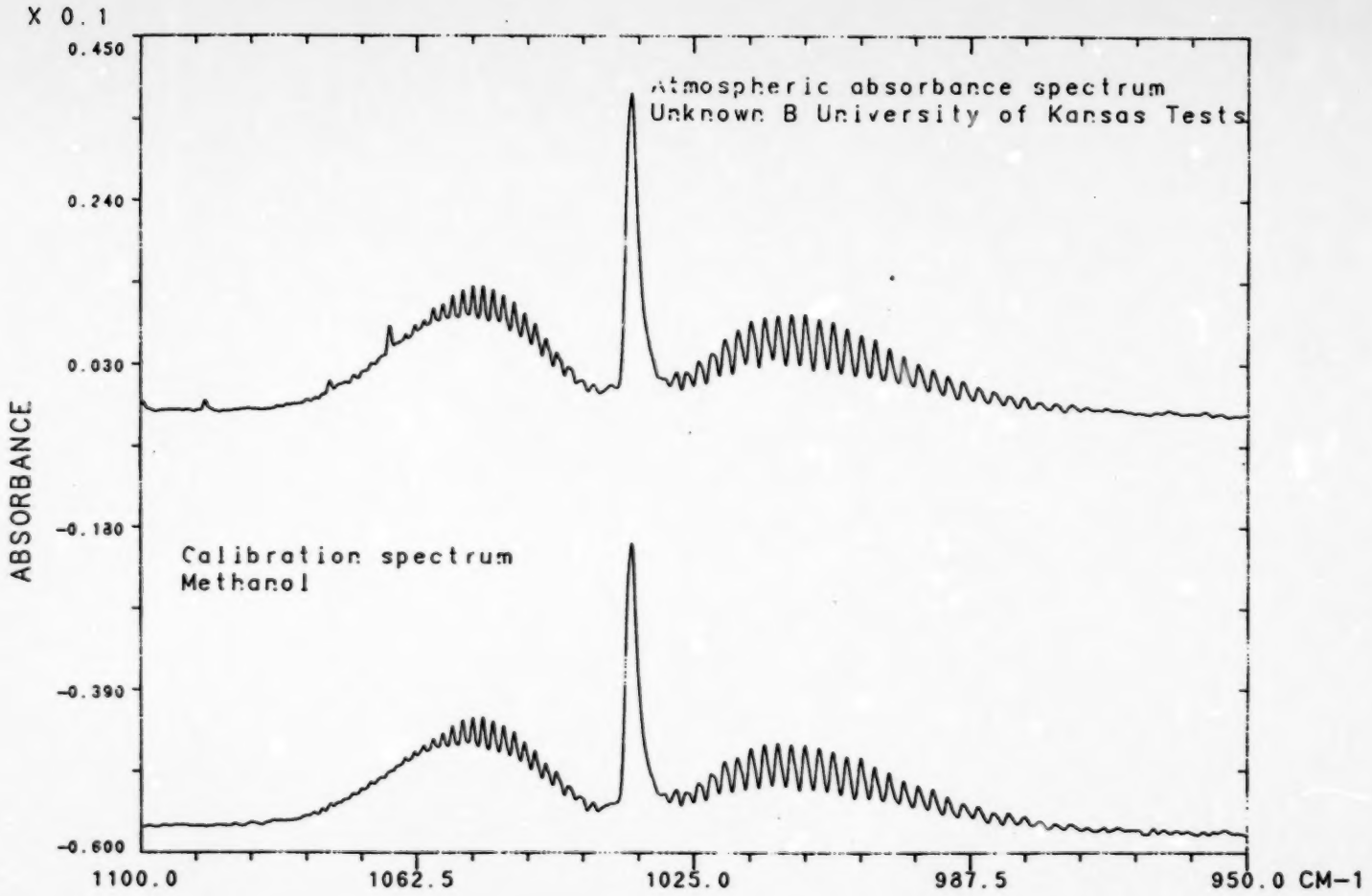

Figure A-2. Unknown Sample B (Methanol). Kansas University tests for EPA testing 5-17-89, 100 meter source 0.1 cm^{-1} res. Reference unknovns 11:45 a.m., unknown B.

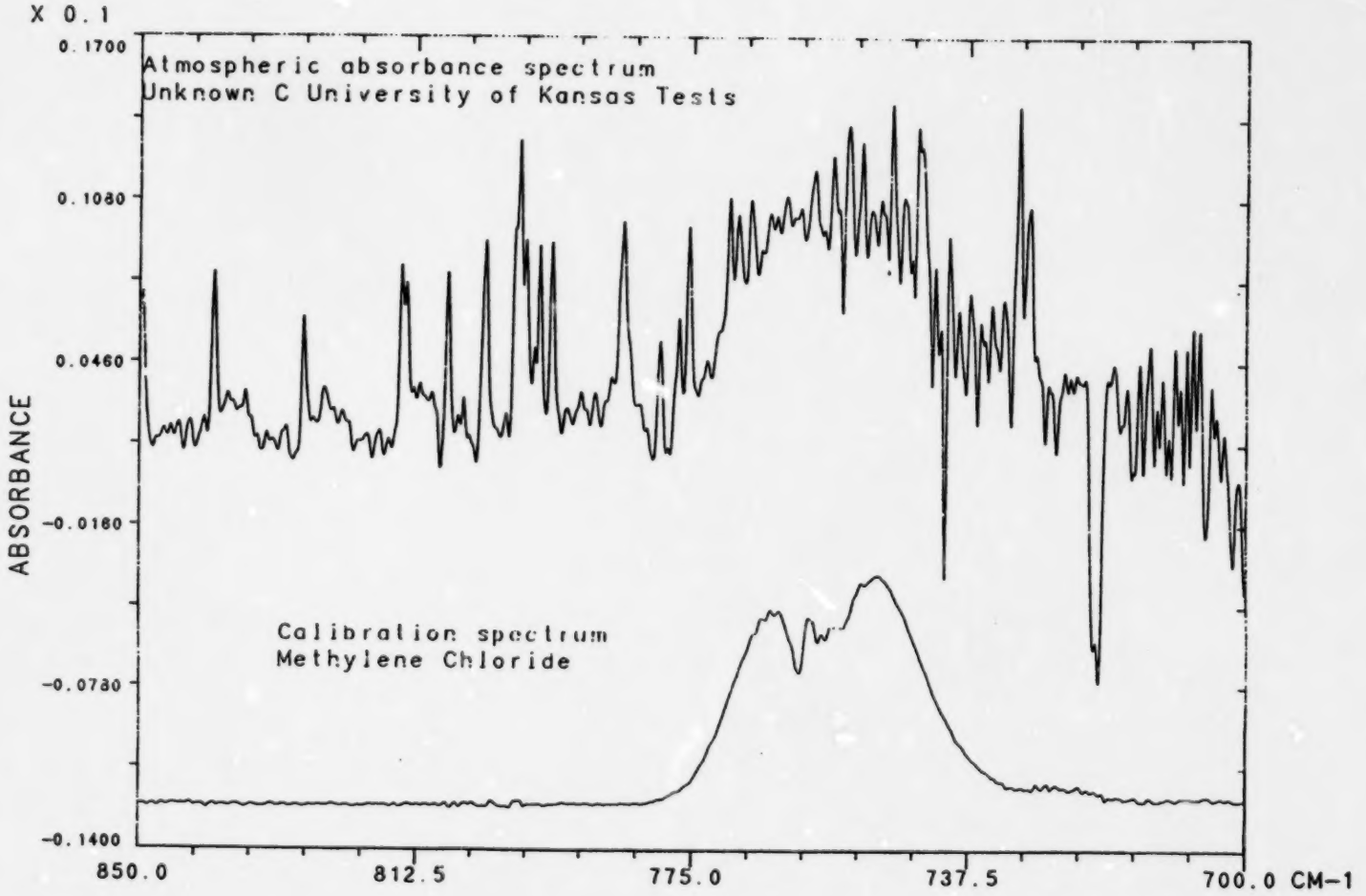

Figure A-3. Unknown Sample C (Methylene chloride). Kansas University tests for EPA testing 5-16-89, 760 feet source 0.1 cm^{-1} res. unk. comp. C.

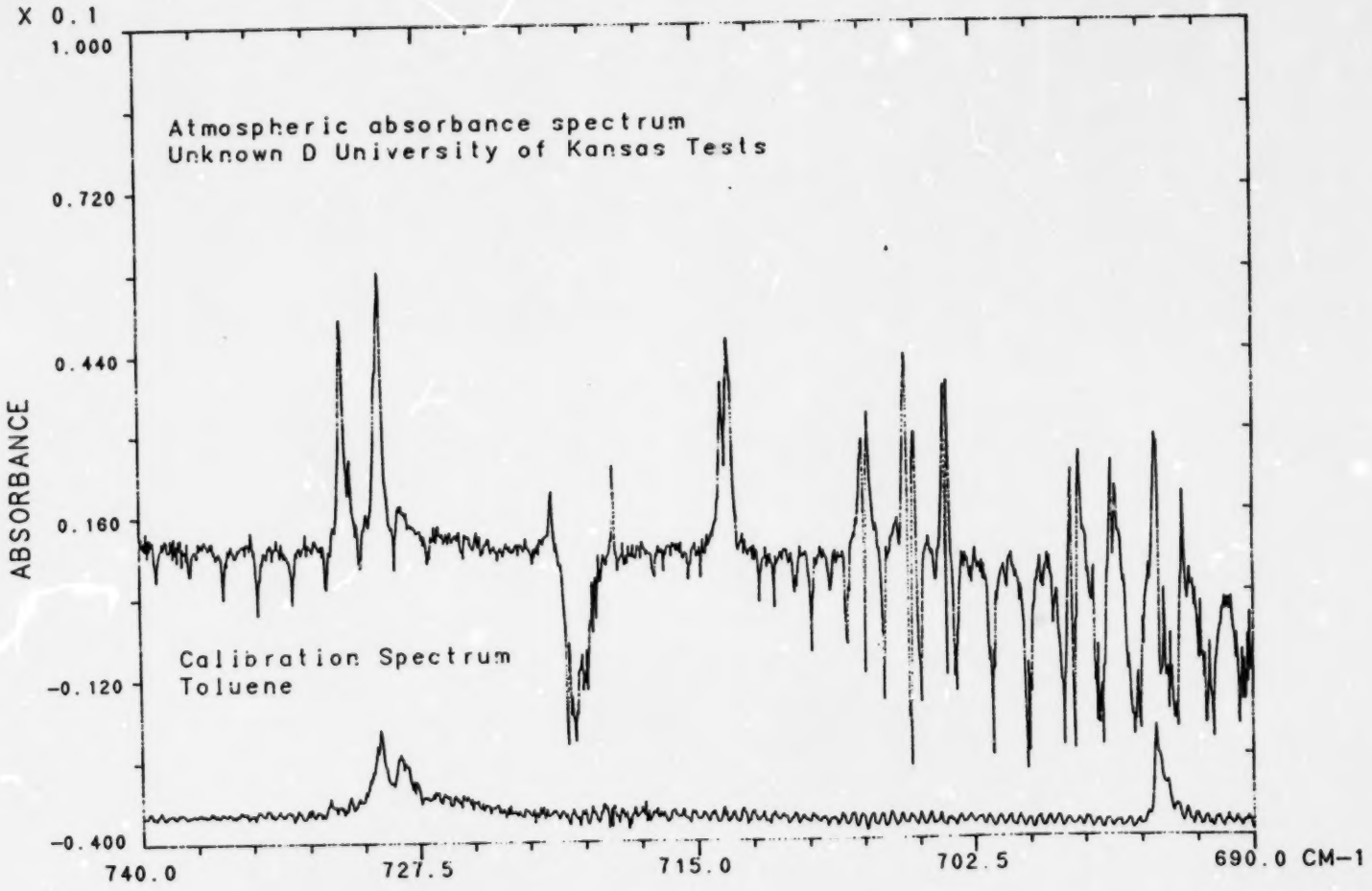

Figure A-4. Unknown Sample D (Toluene). Kansas University tests for EPA testing 5-17-89, 100 meter source 0.1 cm^{-1} res. Reference unknowns 12:45 p.m., unknown D.

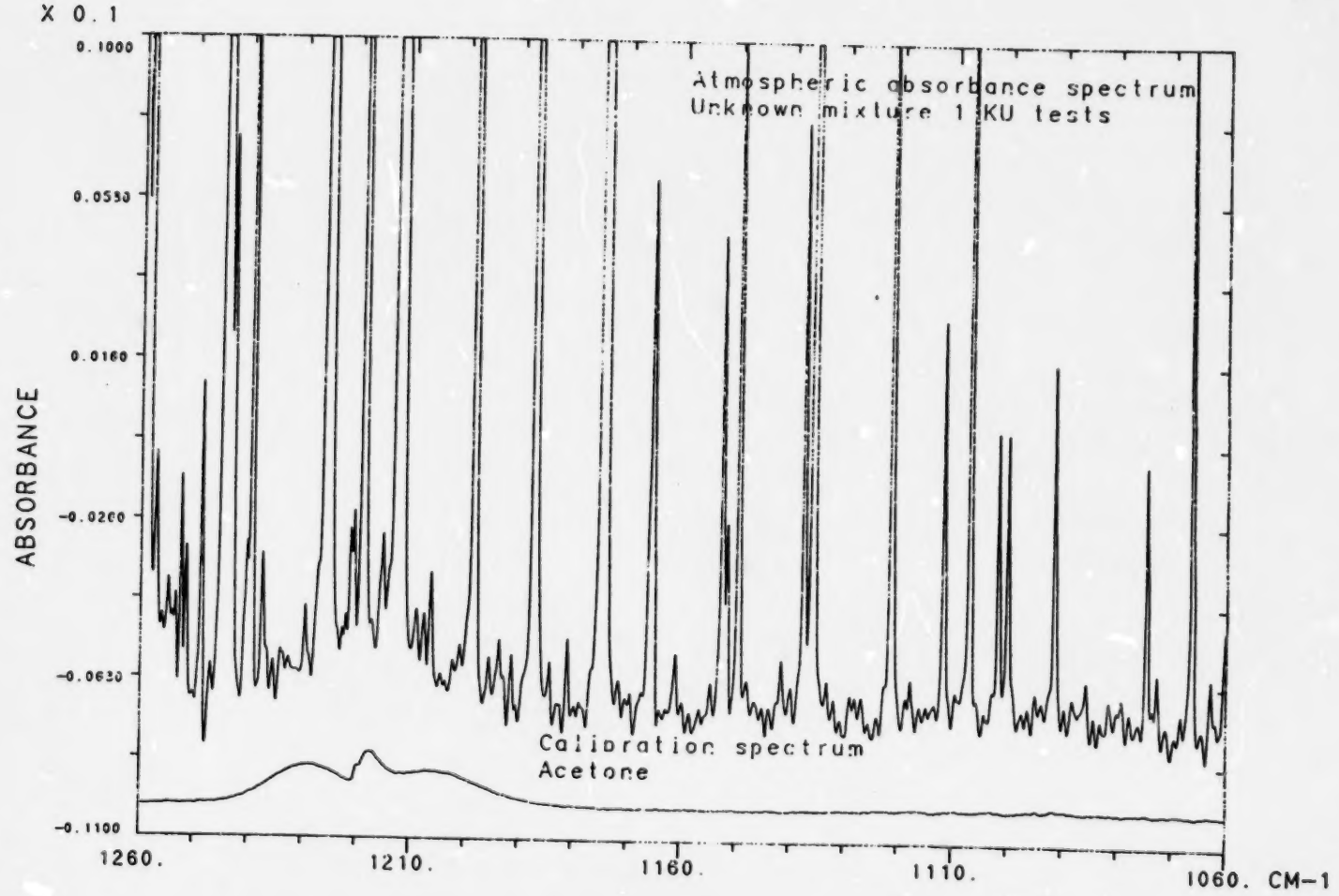

Figure A-5. Unknown Mixture 1. Kansas University tests for EPA testing 5-17-89, 100 meter source 0.1 cm^{-1} res. Reference unknowns 2:11 p.m., mixture 1.

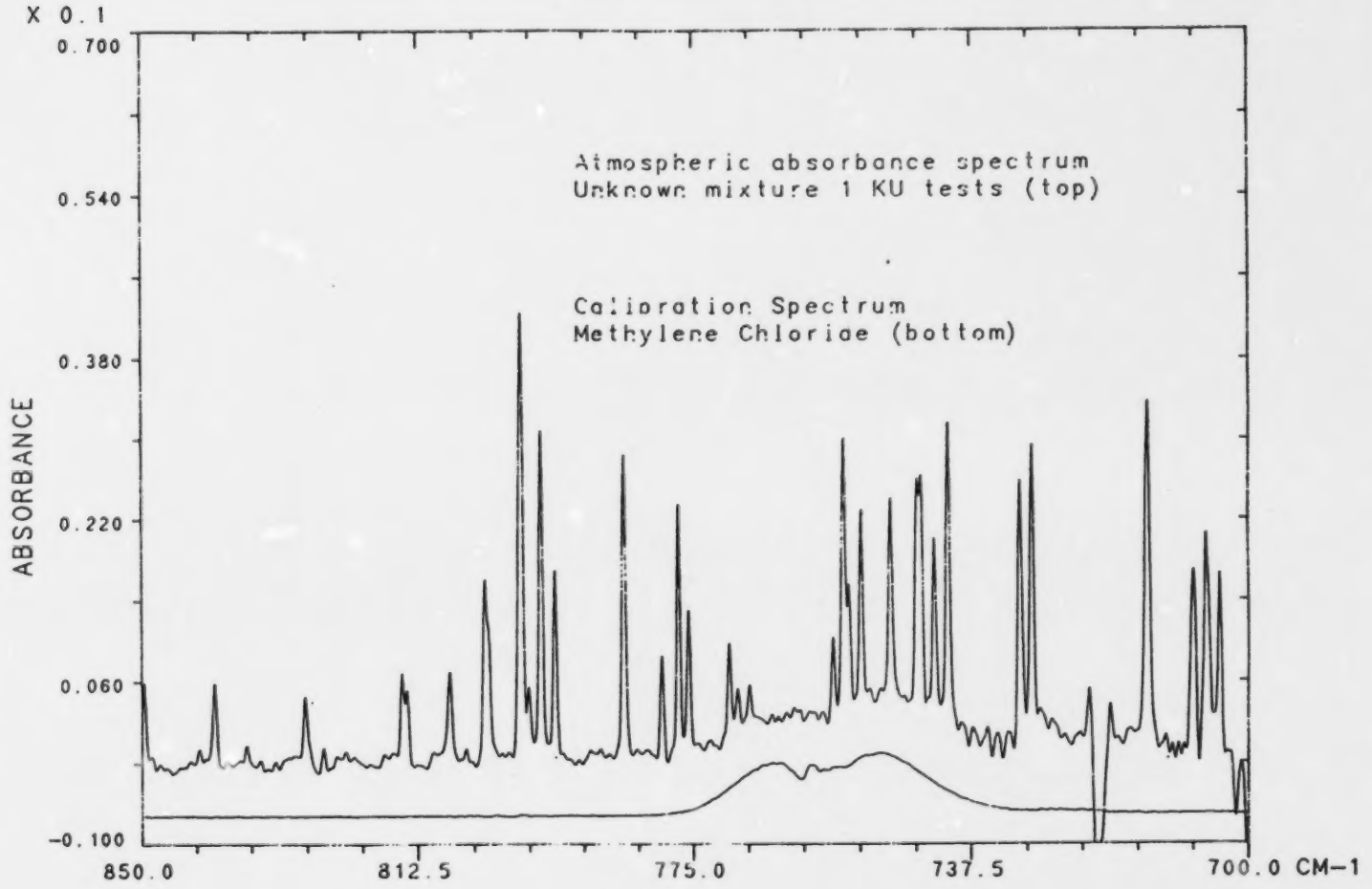

Figure A-6. Unknown Mixture 1. Kansas University tests for EPA testing 5-17-89, 100 meter source 0.1 cm^{-1} res. Reference unknowns 2:11 p.m., mixture 1.

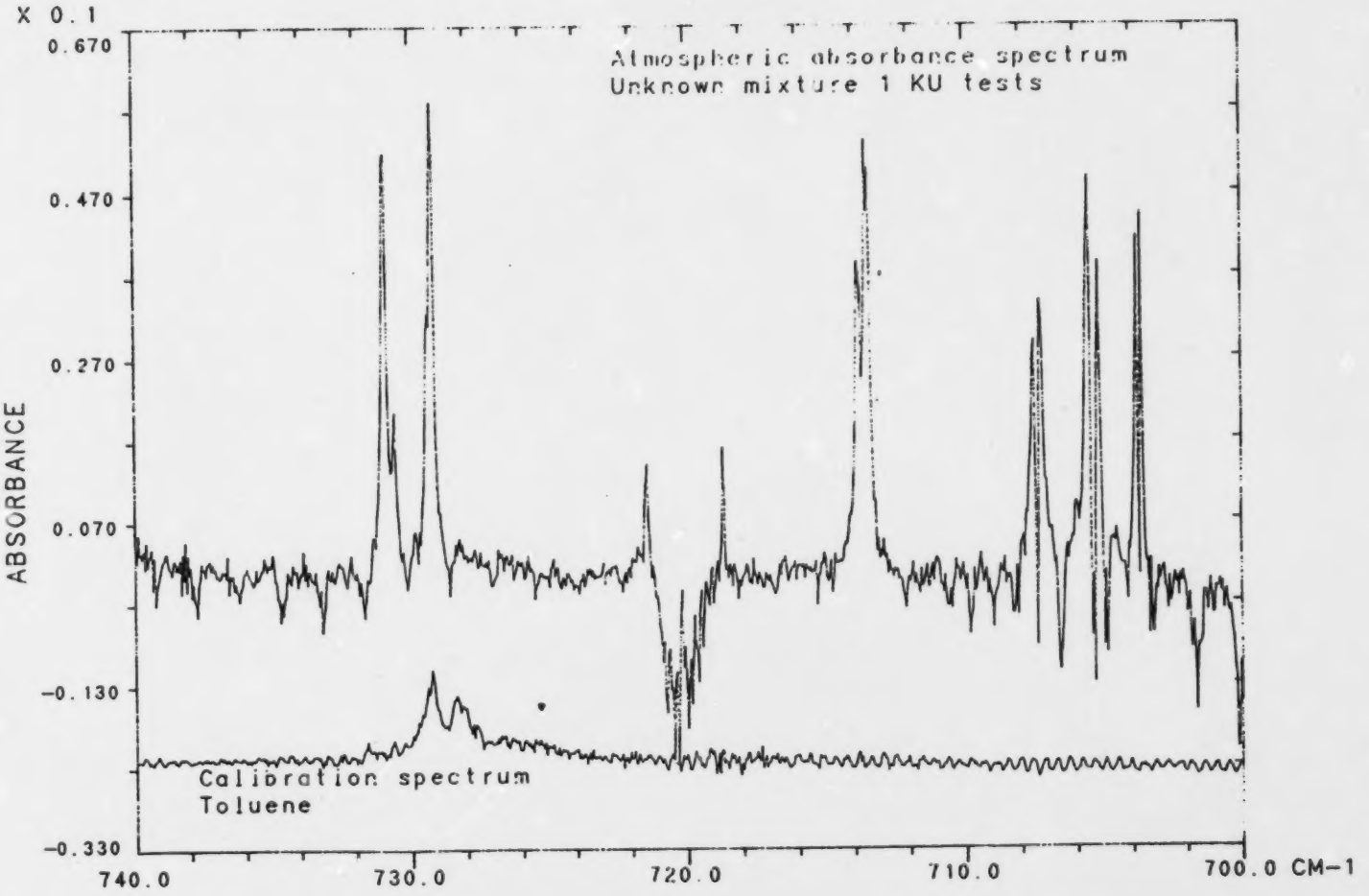

Figure A-7. Unknown Mixture 1. Kansas University tests for EPA testing 5-17-89, 100 meter source 0.1 cm^{-1} res. Reference unknowns 2:11 p.m., mixture 1.

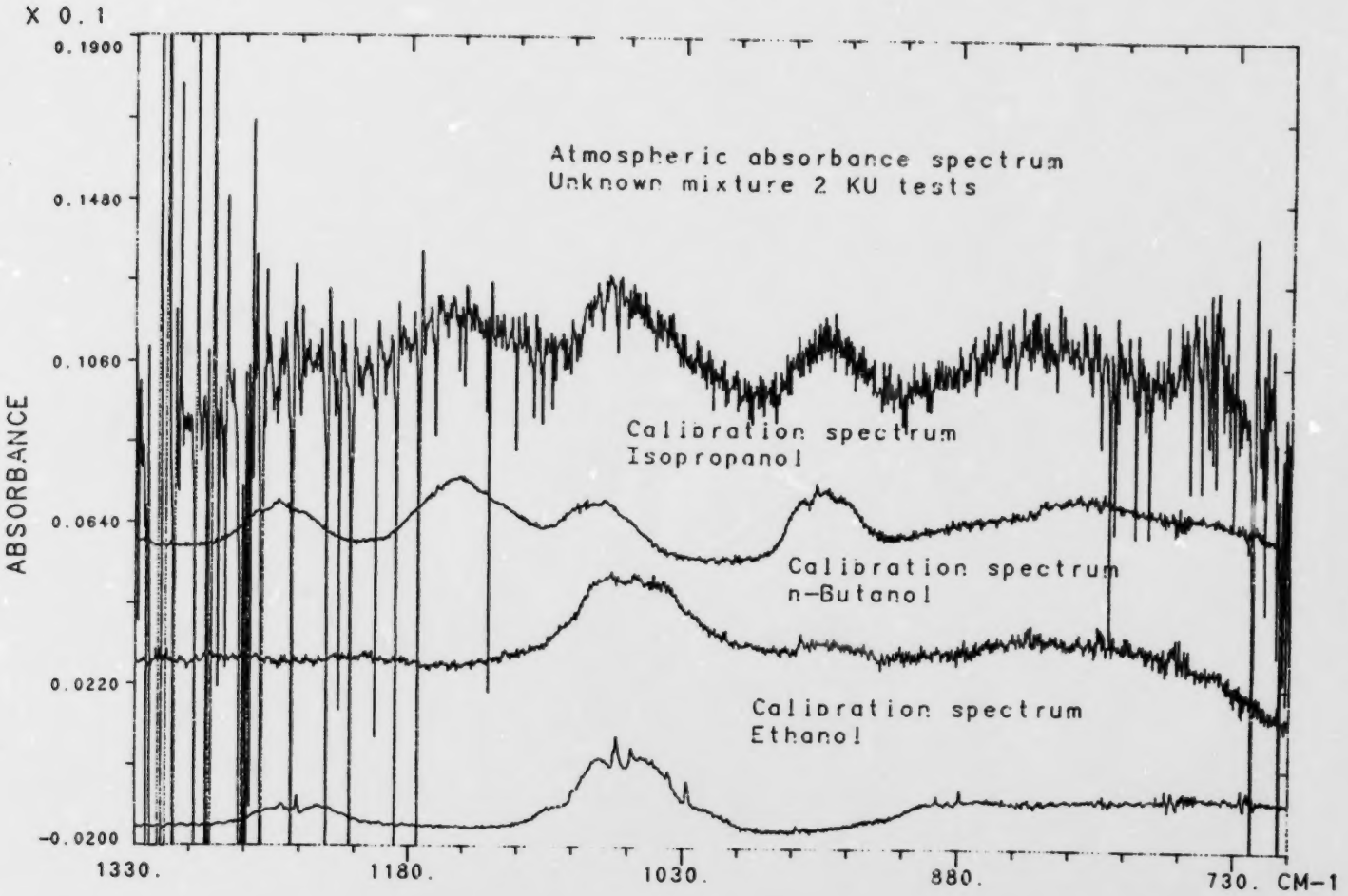

Figure A-8. Unknown Mixture 2. Kansas University tests for EPA testing 5-19-89, 100 meter source 0.1 cm^{-1} res. Phase work 57-58 counts Mixture 2.

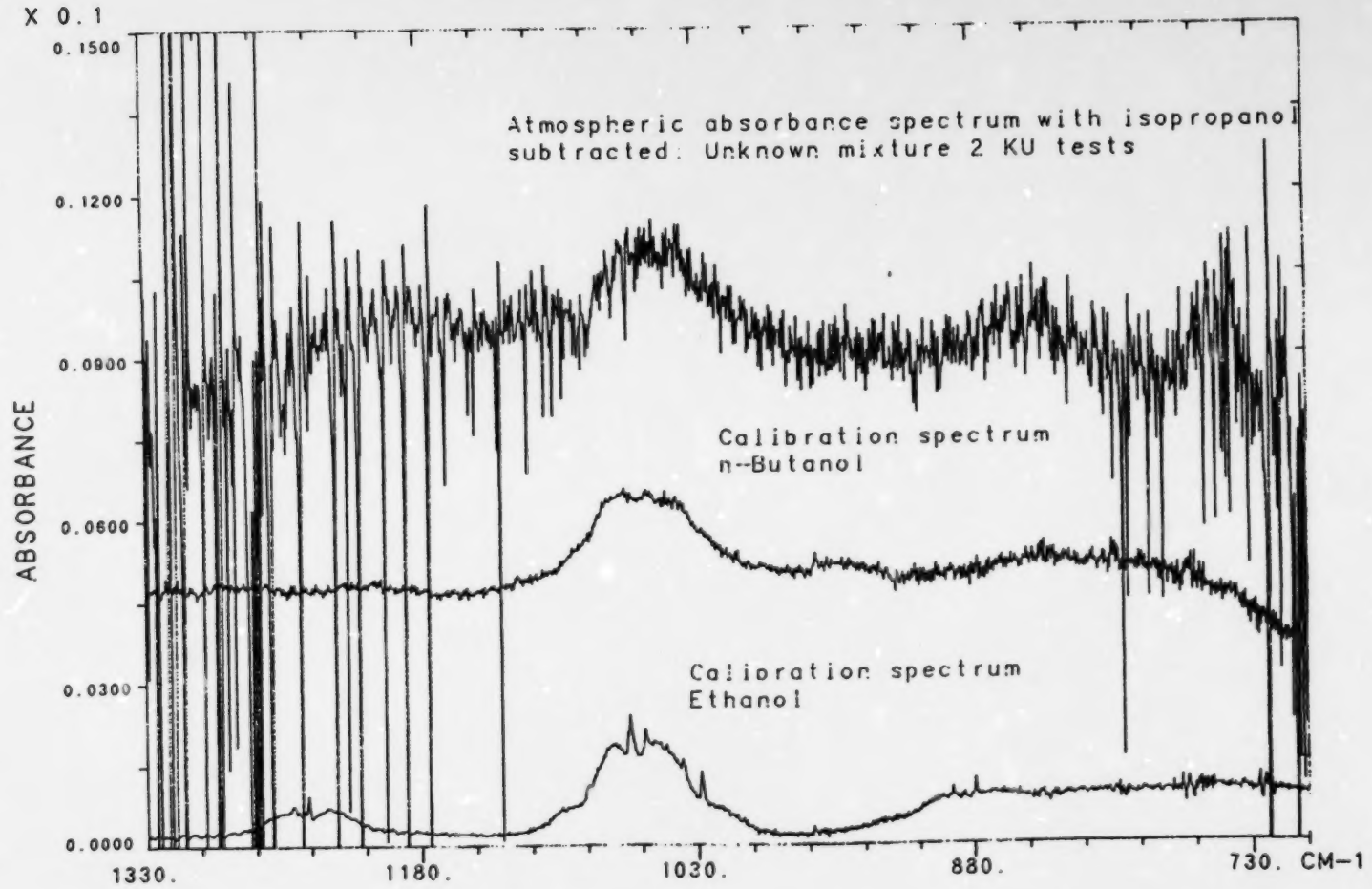

Figure A-9. Unknown Mixture 2. Kansas University tests for EPA testing 5-19-89, 100 meter source 0.1 cm^{-1} res. Phase work 57-58 counts Mixture 2.

ANALYSIS OF UNKNOWN MIXTURE 4

Three compounds were reported to be present in Mixture 4, again two compounds were easily recognized (methylene chloride and 1,1,1-trichloroethane). The third compound was toluene at a concentration which was not detectable at these path lengths.

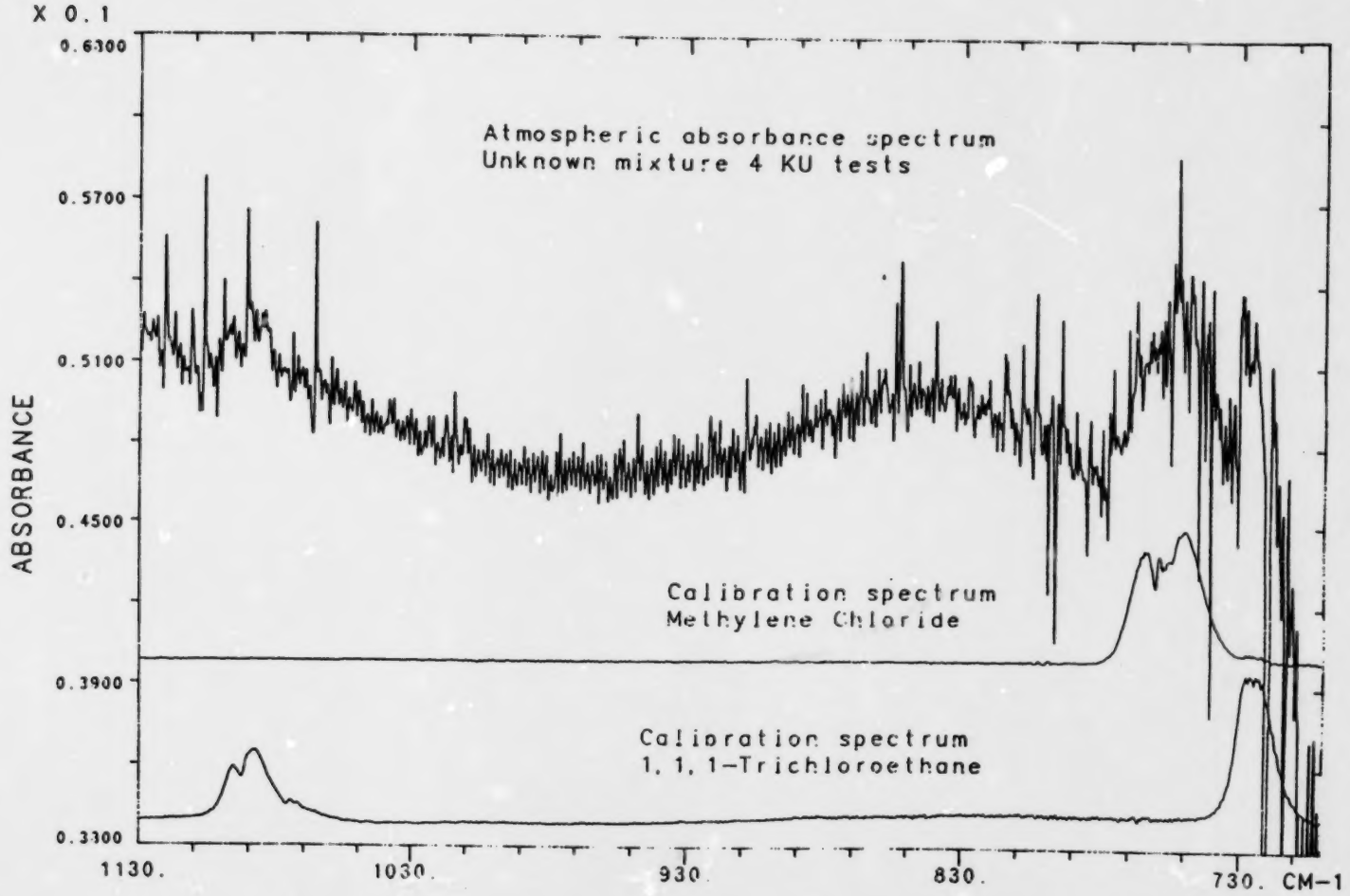

Figure A-10. Unknown Mixture 4. Kansas University tests for EPA testing 5-19-89, 100 meter source 0.1 cm^{-1} res. Phase work 57-58 counts, mixture 4.

APPENDIX B

SPECTRA FROM FIELD WORK AT SITE A

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DISCUSSION OF SITE A

Site A was chosen to test the field reliability of the mobile FT-IR spectrometer system. Site A was analyzed in four different places in four days. There was a large amount of data generated from this site and just a fraction of it will be reviewed here. The site was expected to contain a high concentration of aliphatic hydrocarbons with little or no substituent groups, i.e., chlorine, and a reasonable amount of aromatics, i.e., benzene, toluene. Analyses of a few spectra are included here.

ANALYSIS OF ABSORBANCE SPECTRA OVER DITCH, SITE A

The following spectra in Figure B-1 show an atmospheric spectrum and two calibrated spectra. The absorbance spectrum was produced by taking the ratio

of the downwind to the upwind of the ditch on Site A. As can be seen below, in the sample, there are two compounds whose structure looks as if it would fit the atmospheric spectrum. However, after further analysis we find n-hexane is probably not a component of this atmospheric spectrum. Isobutane or a compound with a very similar chemical structure does appear to be present, this can be seen in Figure B-2. The isobutane subtracted out of the sample spectrum nicely and the resultant spectrum now no longer resembles the n-hexane especially at ~2885 cm^{-1}. This spectra could then be further matched if need be.

ANALYSIS OF ABSORBANCE SPECTRUM USING SPECTRA FROM TWO SITES ON SITE A

Two spectra from different places at Site A were ratioed to give the following absorbance spectrum, Figure B-3. The resultant spectrum displays a band due to benzene which is compared against the benzene calibration spectrum. Both places in which the single beam spectra were taken had benzene present, the resultant band intensity is thus decreased when the spectra are ratioed.

EMISSION FROM A HOT STACK DOWNWIND OF SITE A

The spectrometer can be turned skyward to use the heat of a smoke stack as a source. With this heat also, the vibrational-rotational bands of the molecules present are excited to higher energy transitions and when they relax give off radiation as can be seen in Figure B-4. The sharp positive going lines are the emission lines, many of which here are due to CO_2. Further analysis will be done with this and similar spectra for emission and absorbance measurements. The stack for this spectrum was located about one mile away.

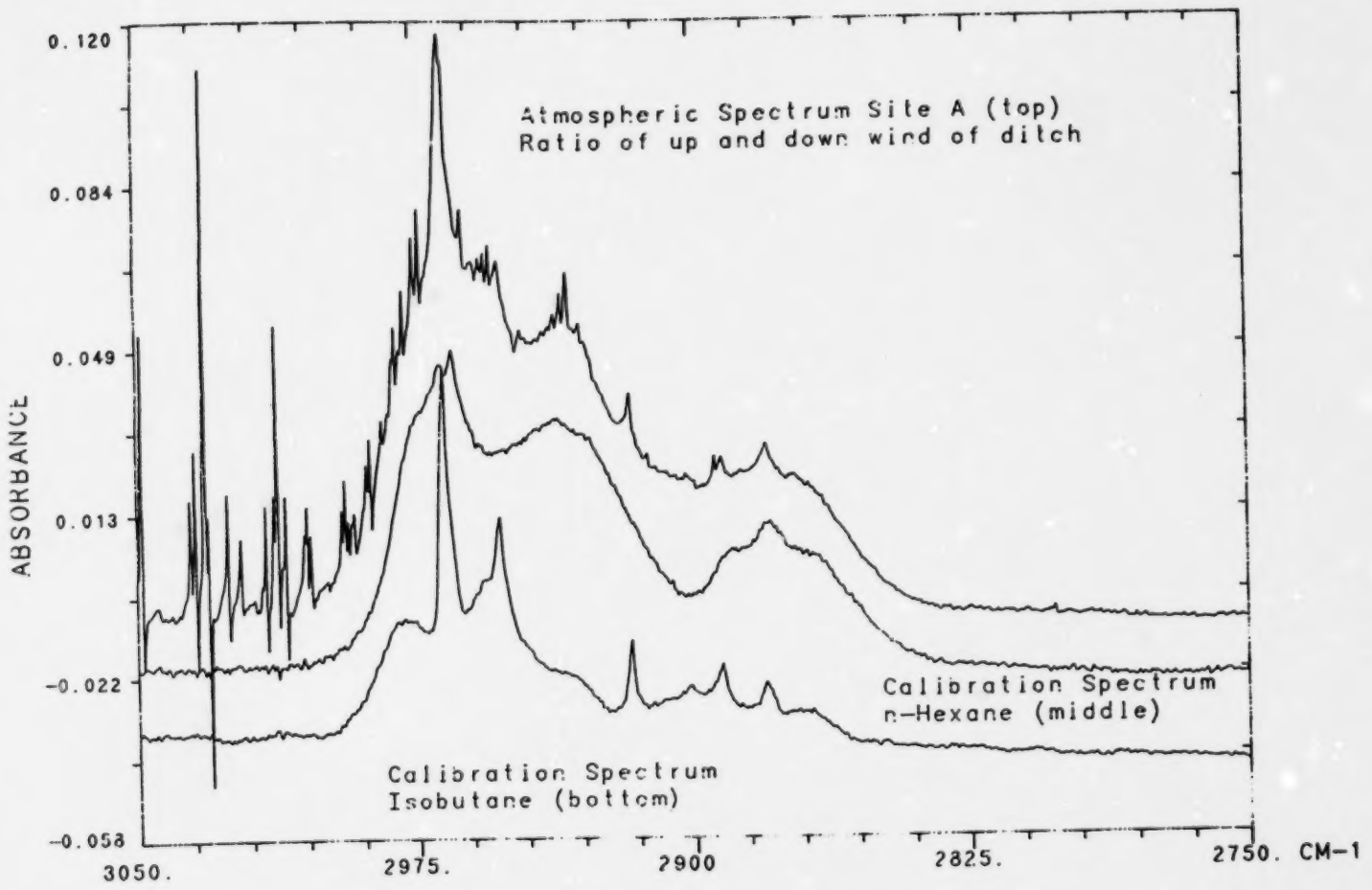

Figure B-1. Atmospheric spectrum Site A; ratio of up and downwind of ditch.

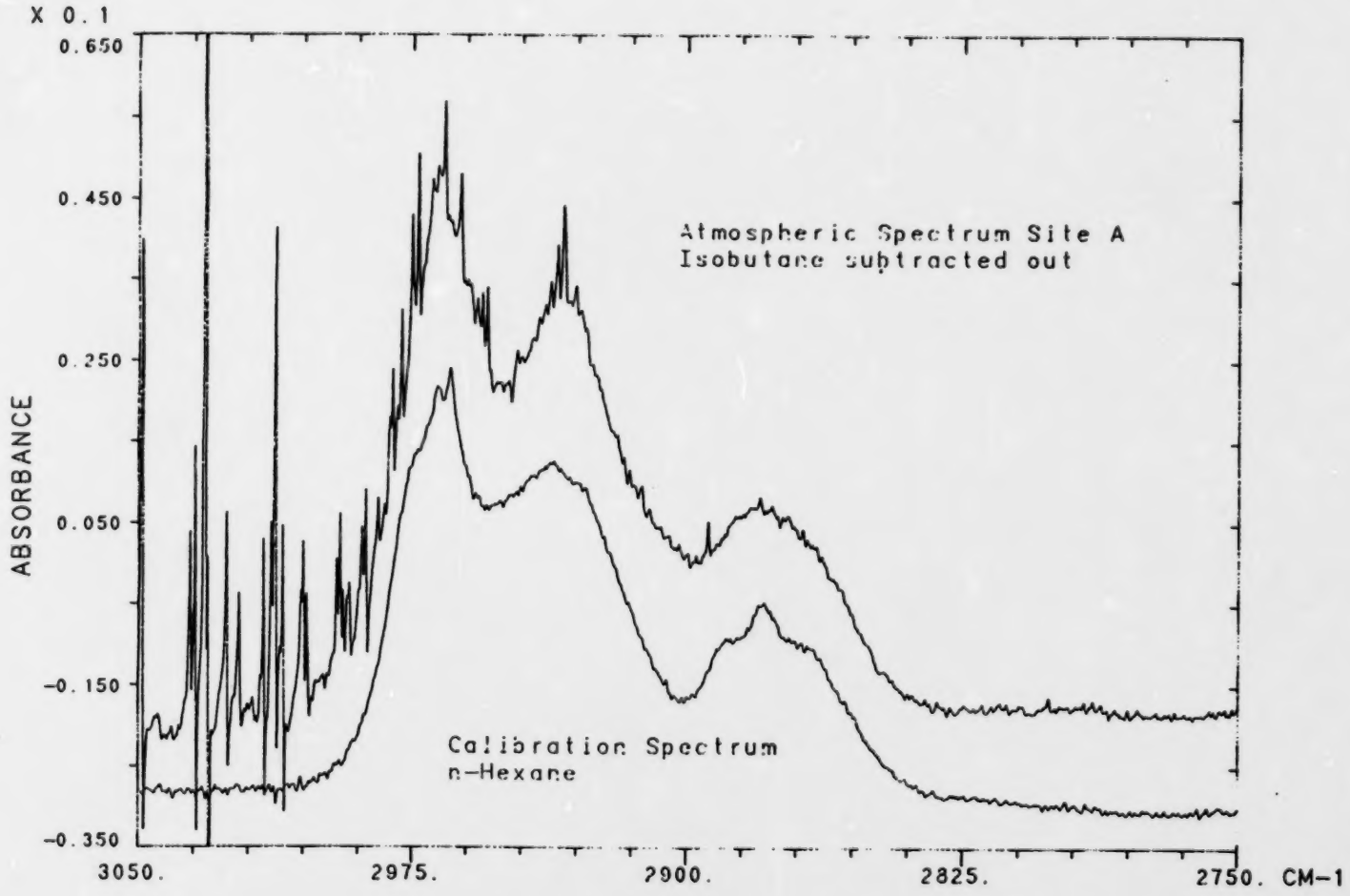

Figure B-2. Atmospheric spectrum Site A; isobutane subtracted out.

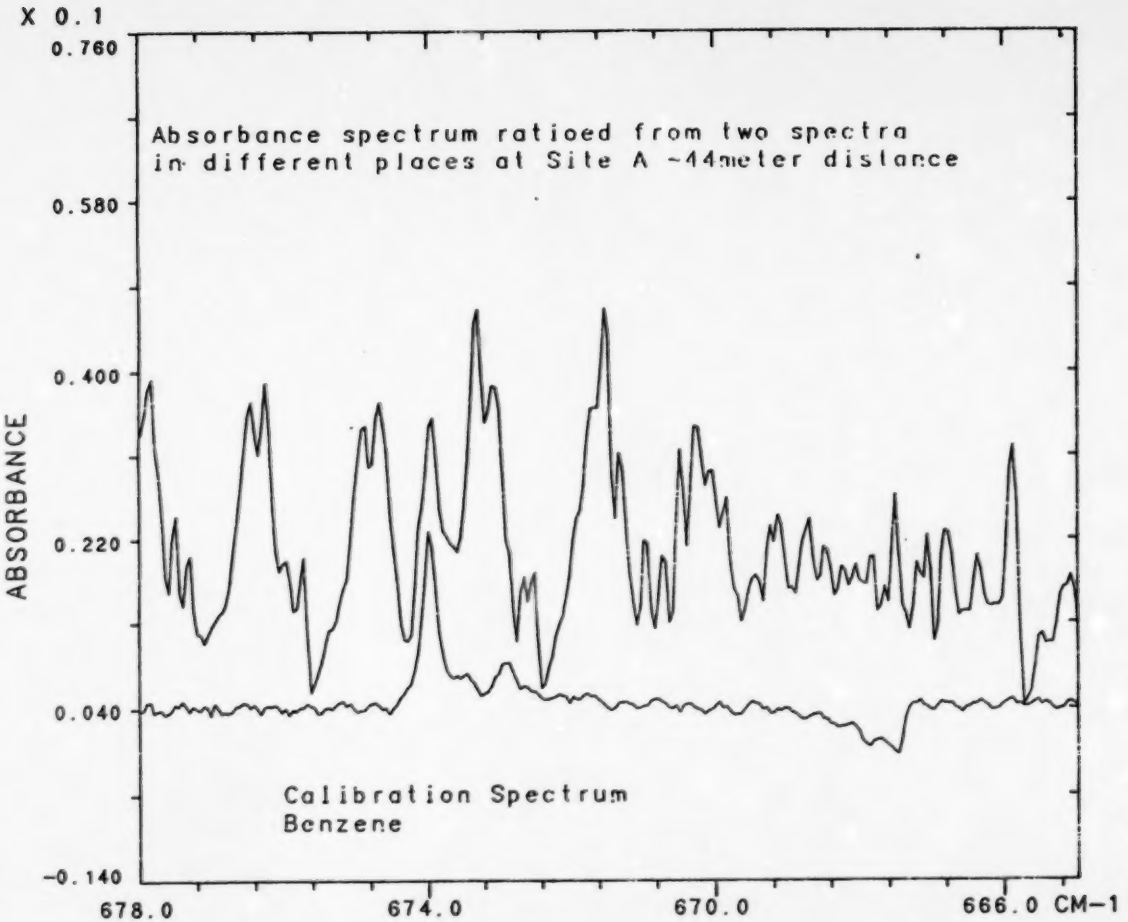

Figure B-3. Absorbance spectrum ratioed from two spectra in different places at Site A ~44 meter distance.

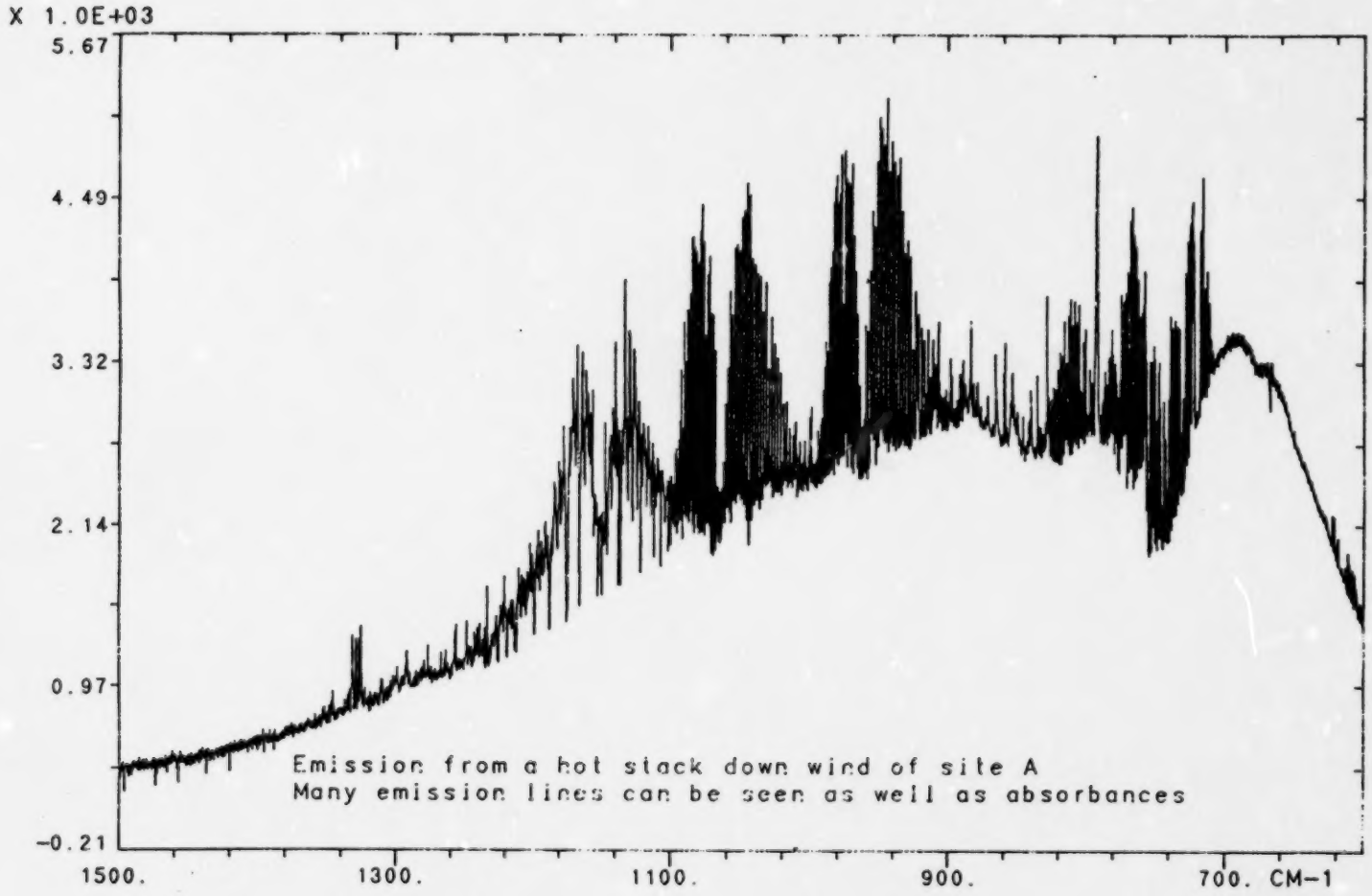

Figure B-4. Emission from a hot stack downwind of Site A.

APPENDIX C

SPECTRA FROM LABORATORY CALIBRATION AND BEER'S LAW PLOTS

This appendix contains the following three figure collections: (1) all calibration spectra in the library at the time of this writing and (2) Beer's Law plots of absorbance versus molar concentration for at least one absorption band from each spectrum in the library with three exceptions (carbon tetrachloride, chloroform, and toluene). For those three compounds there are inconsistencies in the data and additional measurements are needed. (3) 15 Reference spectra of 13 compounds that were taken in preparation for Site A. A listing of the compounds showing the page number for the figures for each compound follows.

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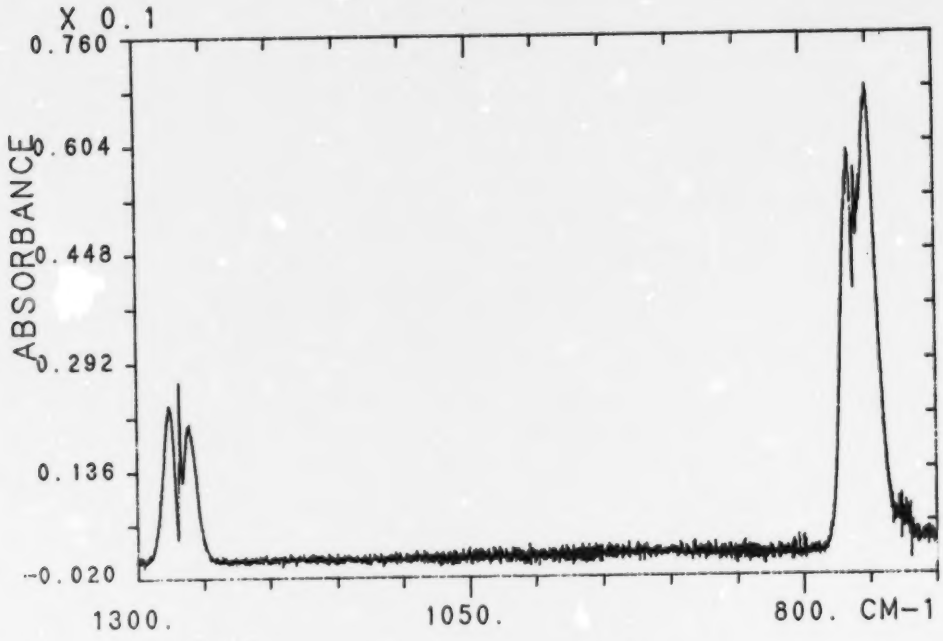

Figure C-1. Calibration of spectrometer at .255 torr for methylene chloride. Source 25 cm from aperture and 16 cm cell 742.2 torr N2.

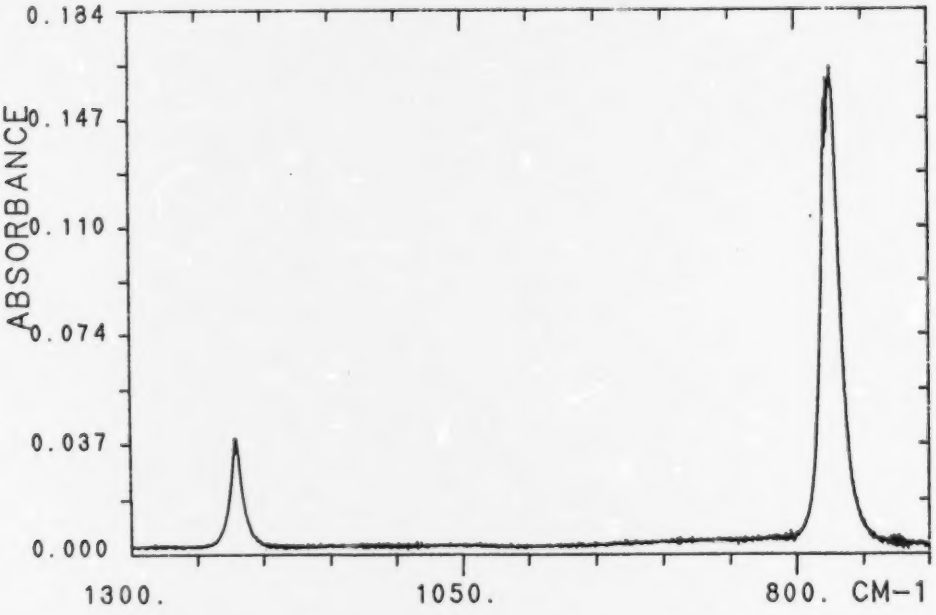

Figure C-2. Calibration of spectrometer at .2055 torr for chloroform. Source 25 cm from aperture and 16 cm cell 739.0 torr N2.

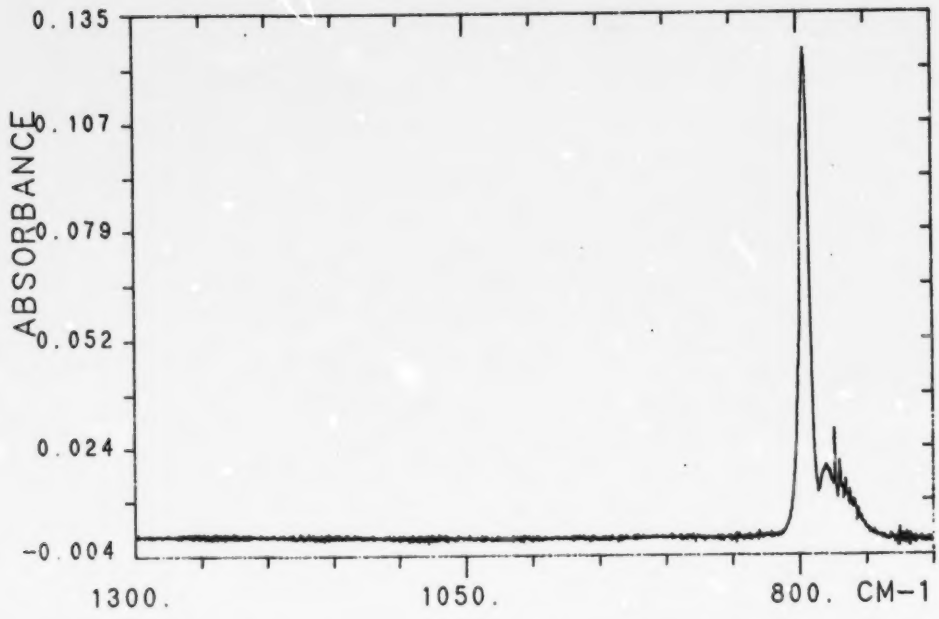

Figure C-3. Calibration of spectrometer at .1014 torr for carbon tetrachloride. Source 25 cm from aperture and 16 cm cell 740.0 torr N2.

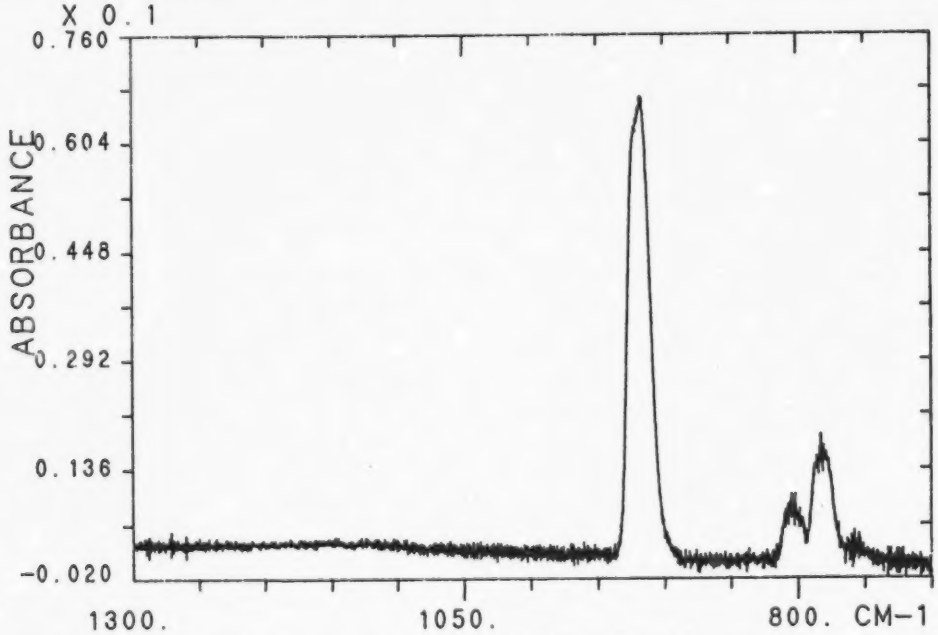

Figure C-4. Calibration of spectrometer for tetrachloroethylene at .2134 torr. Source 25 cm from aperture and 16 cm cell 741.1 torr.

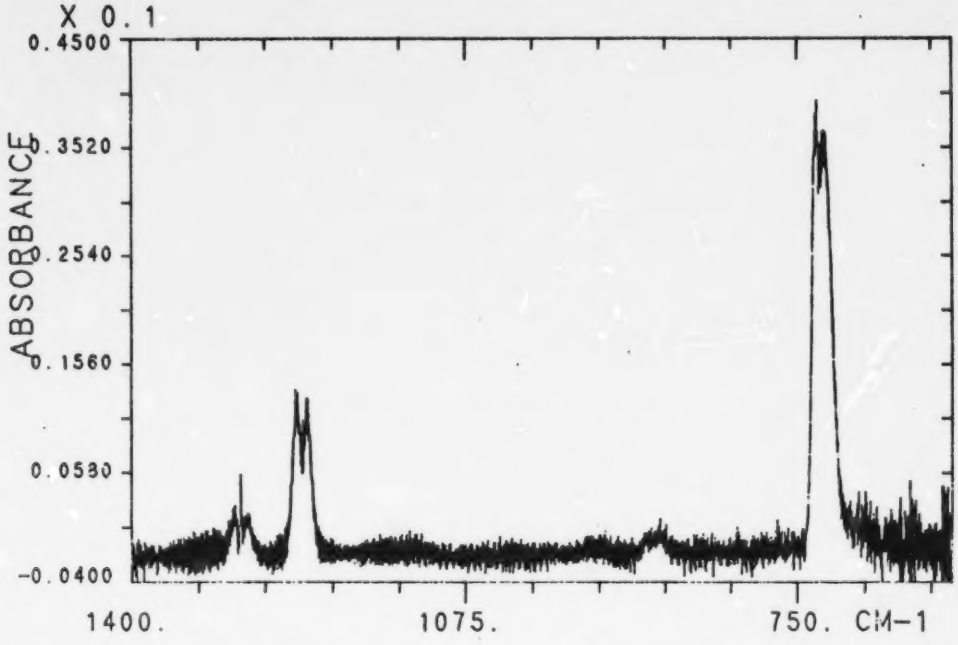

Figure C-5. Calibration of spectrometer for 1,2-dichloroethane at .2292 torr. Source 25 cm from aperture and 16 cm cell 739.7 torr.

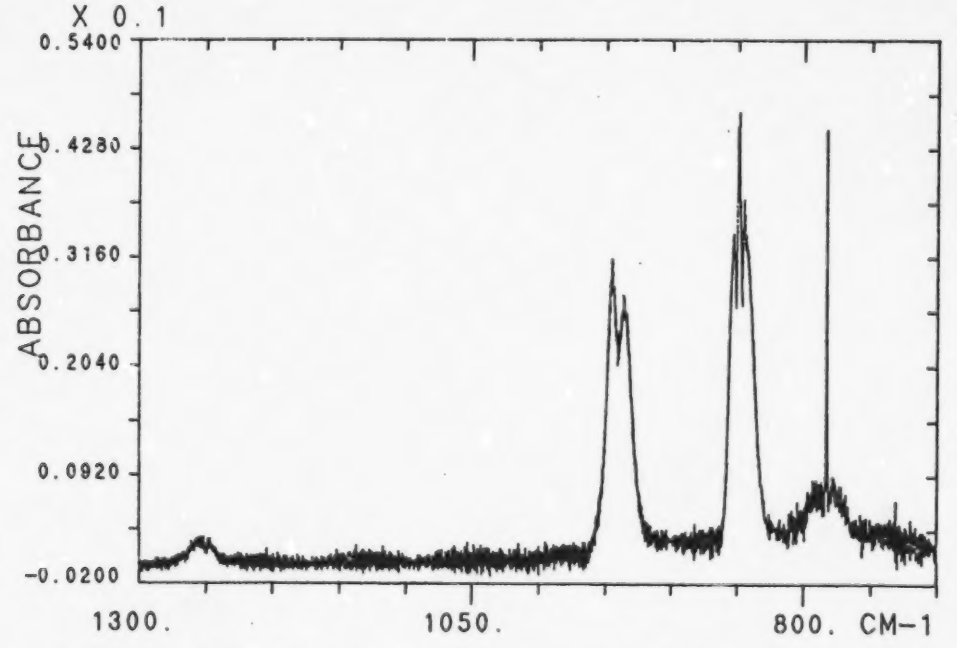

Figure C-6. Calibration of spectrometer for trichloroethylene at 0.1564 torr. Source 25 cm from aperture and 16 cm cell 740.0 torr.

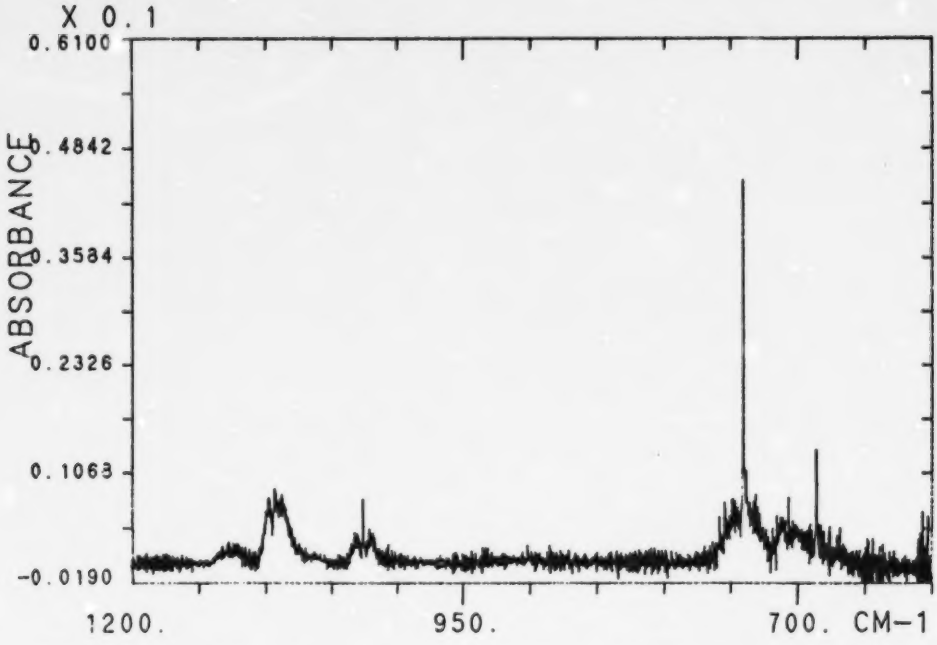

Figure C-7. Calibration of spectrometer for chlorobenzene at 0.0967 torr. Source 25 cm from aperture and 16 cm cell 740.7 torr.

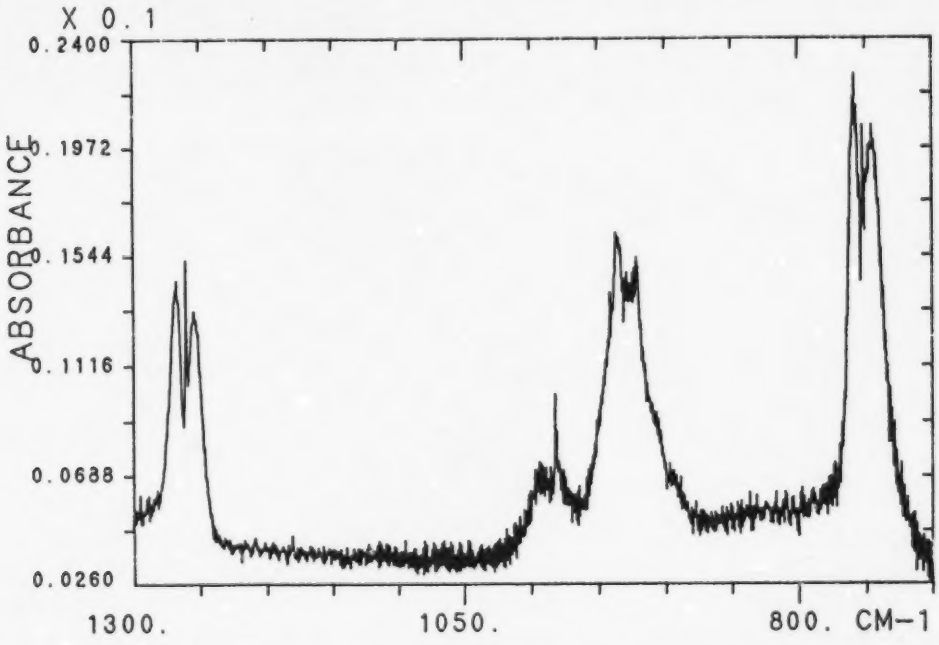

Figure C-8. Calibration of spectrometer for 3-chloropropene at .2325 torr. Source 25 cm from aperture and 16 cm cell 740.1 torr.

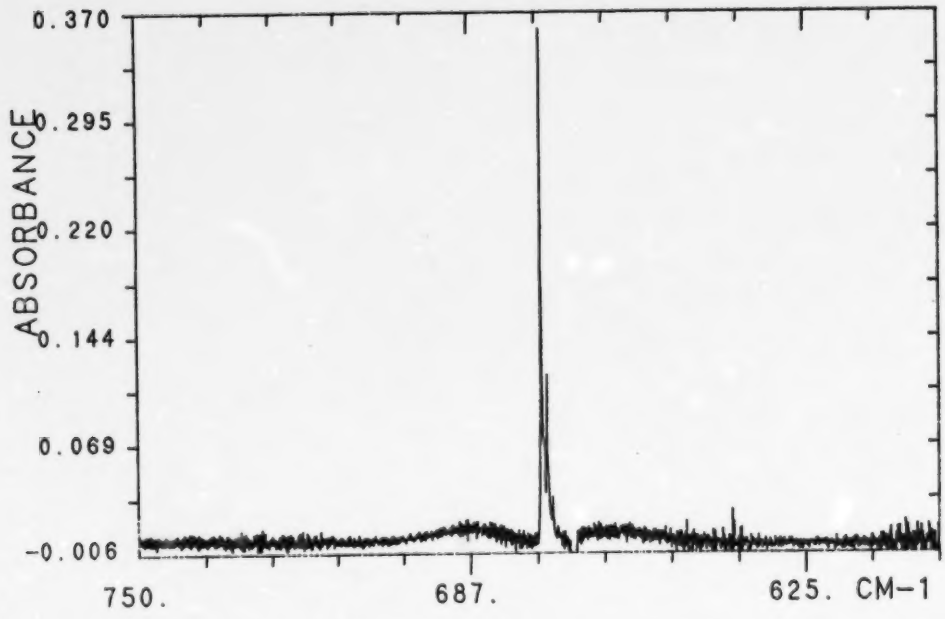

Figure C-9. Calibration of spectrometer for benzene at .1224 torr. Source 25 cm from aperture and 16 cm cell 740.2 torr.

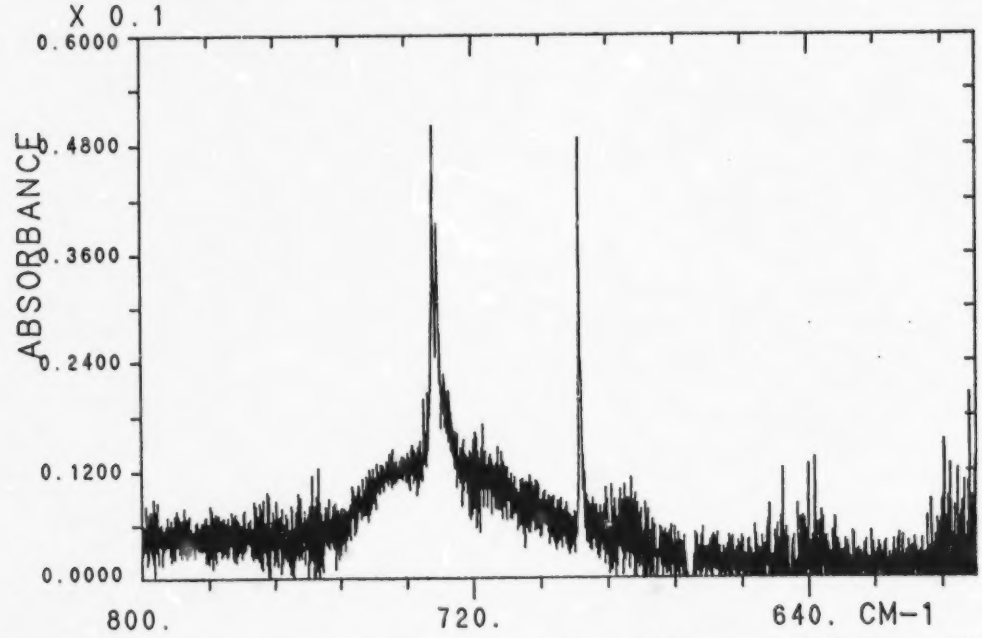

Figure C-10. Calibration of spectrometer for toluene at .1670 torr. Source 25 cm from aperture and 16 cm cell 740.5 torr.

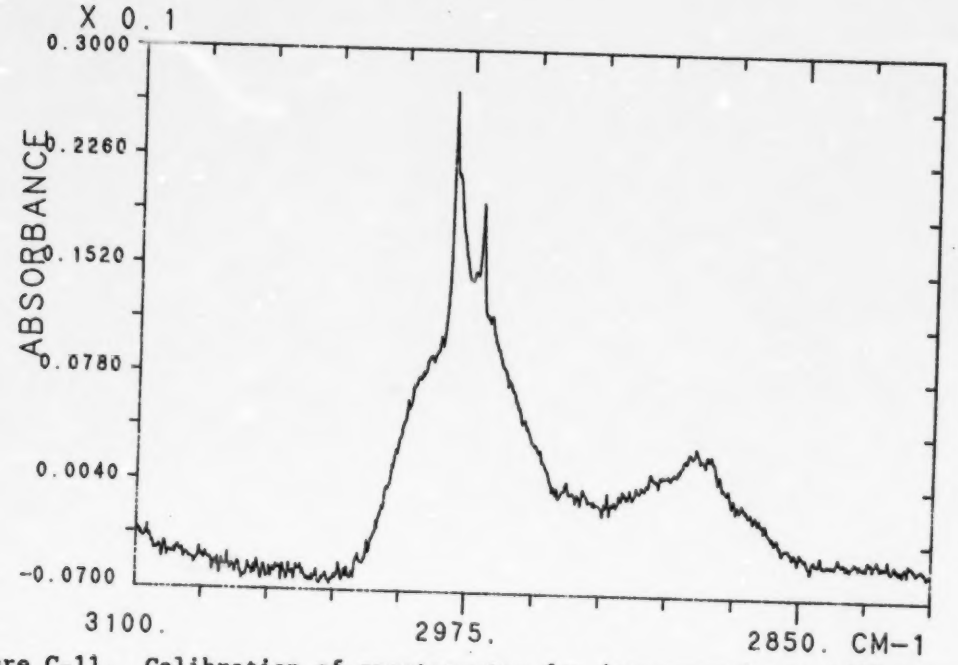

Figure C-11. Calibration of spectrometer for isopropanol at .1603 torr. Source 25 cm from aperture and 16 cm cell 740.0 torr.

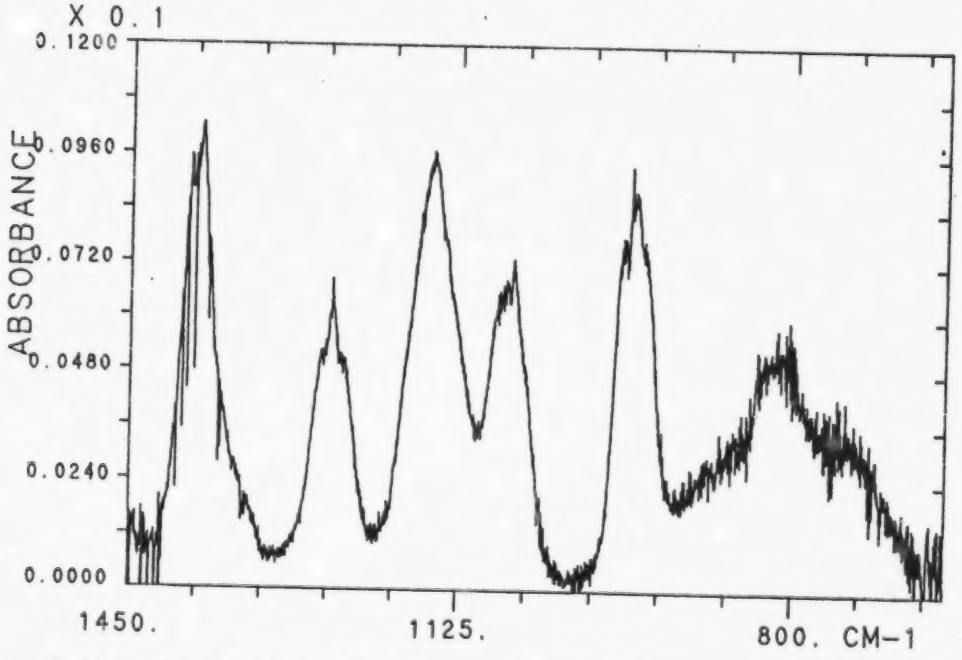

Figure C-12. Calibration of spectrometer for isopropanol at .1603 torr. Source 25 cm from aperture and 16 cm cell 740.0 torr.

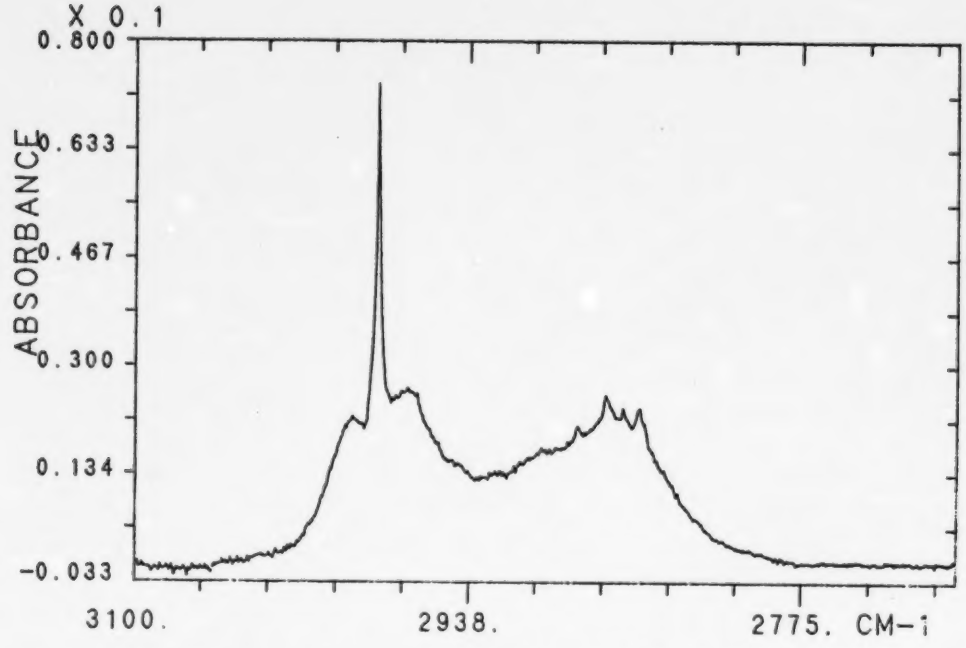

Figure C-13. Calibration of spectrometer for tetrahydrofuran at .1699 torr. Source 25 cm from aperture and 16 cm cell 740.0 torr.

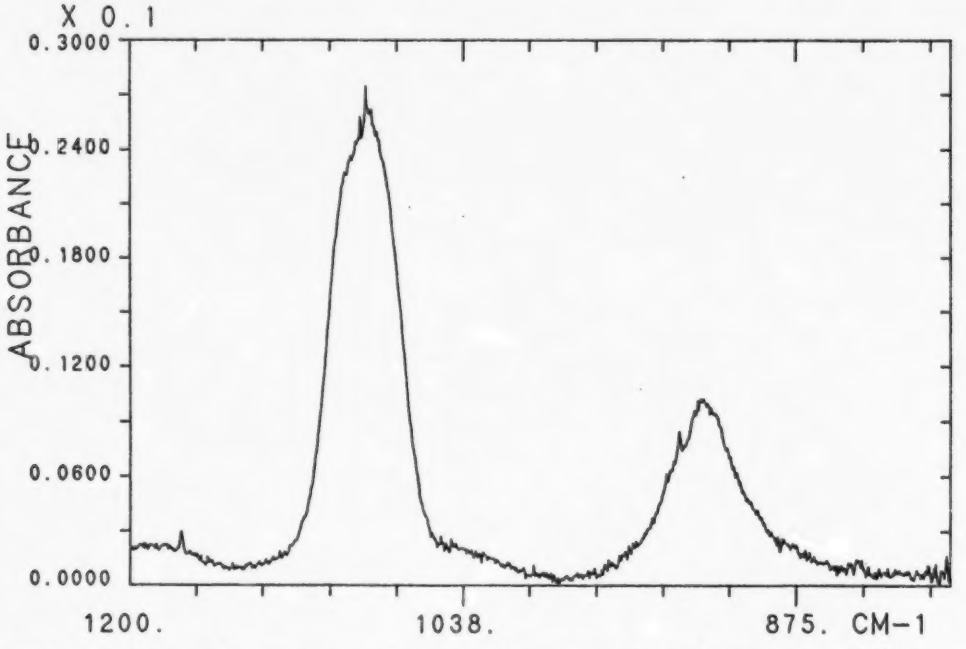

Figure C-14. Calibration of spectrometer for tetrahydrofuran at .1699 torr. Source 25 cm from aperture and 16 cm cell 740.0 torr.

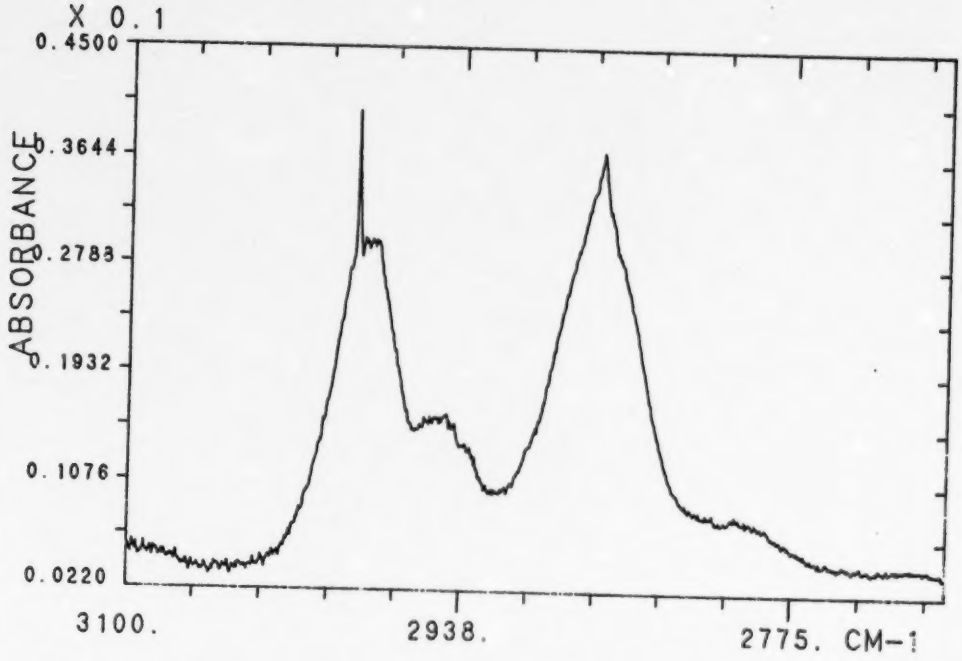

Figure C-15. Calibration of spectrometer for diethyl ether at .1375 torr. Source 25 cm from aperture and 16 cm cell 740.7 torr.

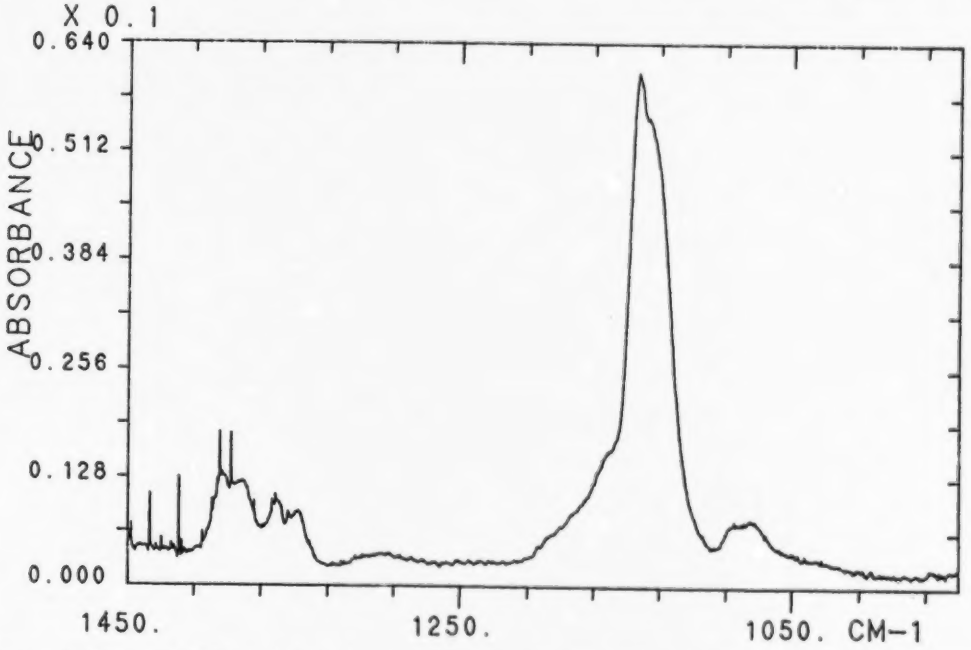

Figure C-16. Calibration of spectrometer for diethyl ether at .1375 torr. Source 25 cm from aperture and 16 cm cell 740.7 torr.

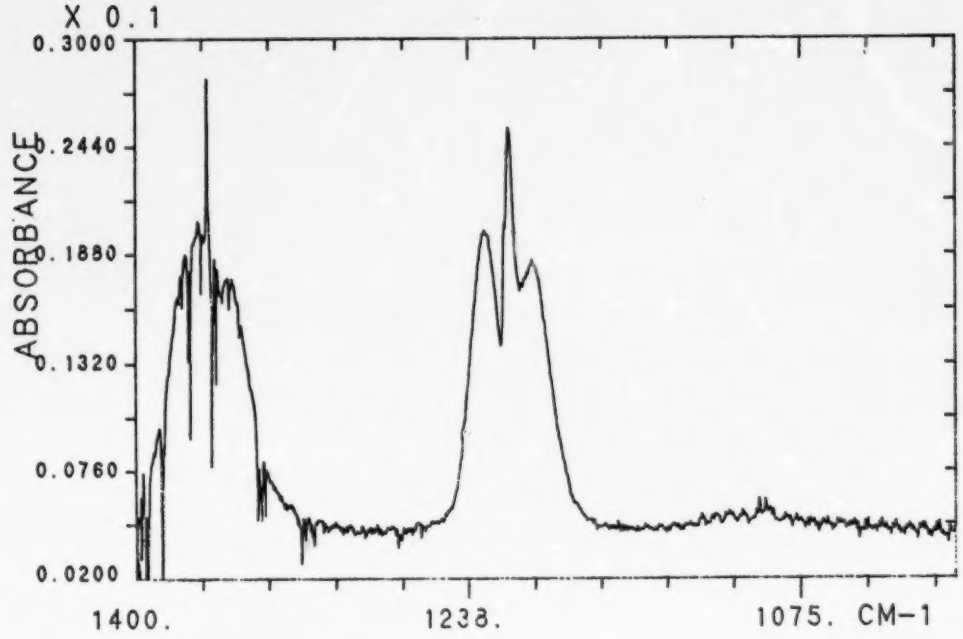

Figure C-17. Calibration of spectrometer for acetone at .1803 torr. Source 25 cm from aperture and 16 cm cell 740.6 torr 23 C.

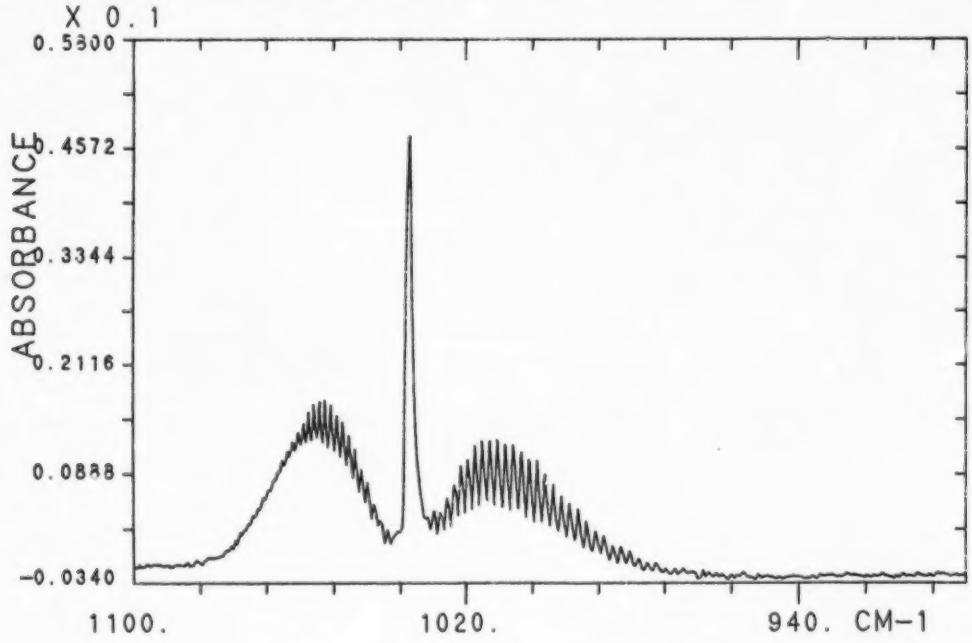

Figure C-18. Calibration of spectrometer for methanol at 0.1372 torr. Source 25 cm from aperture and 16 cm cell 741.1 torr.

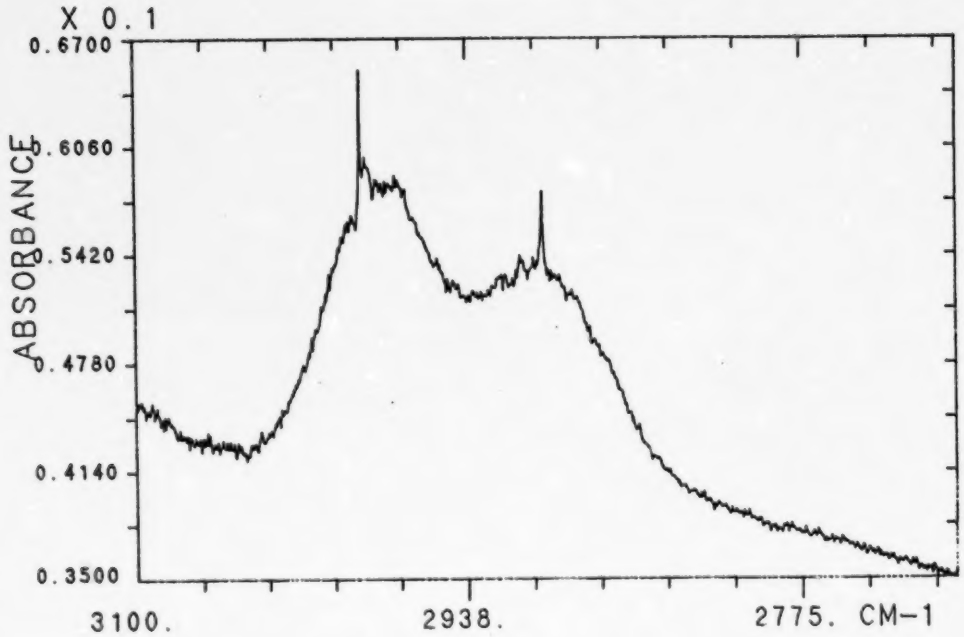

Figure C-19. Calibration of spectrometer for ethanol at .1985 torr. Source 25 cm from aperture and 16 cm cell 740.0 torr.

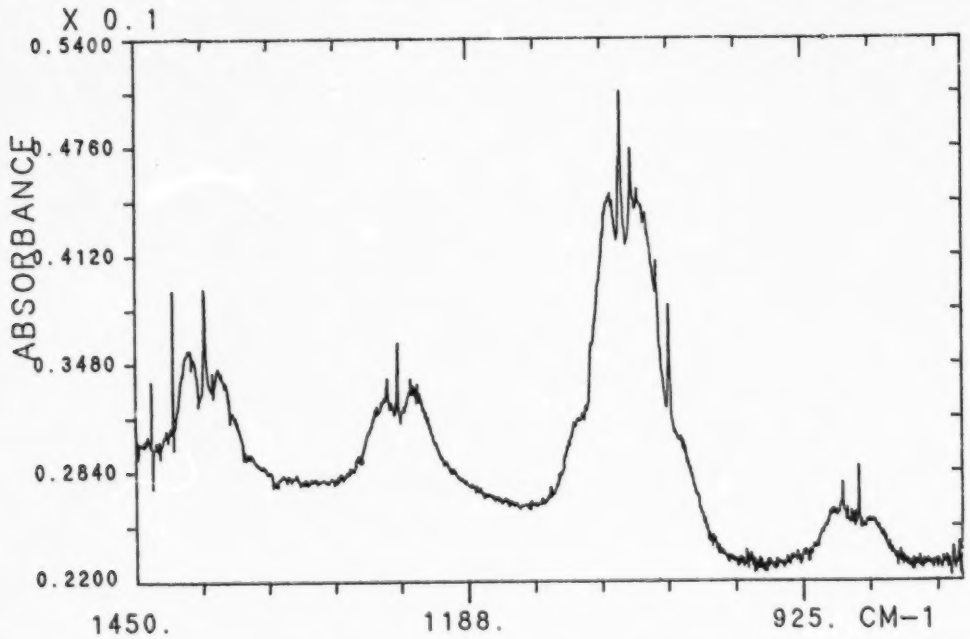

Figure C-20. Calibration of spectrometer for ethanol at .1985 torr. Source 25 cm from aperture and 16 cm cell 740.0 torr.

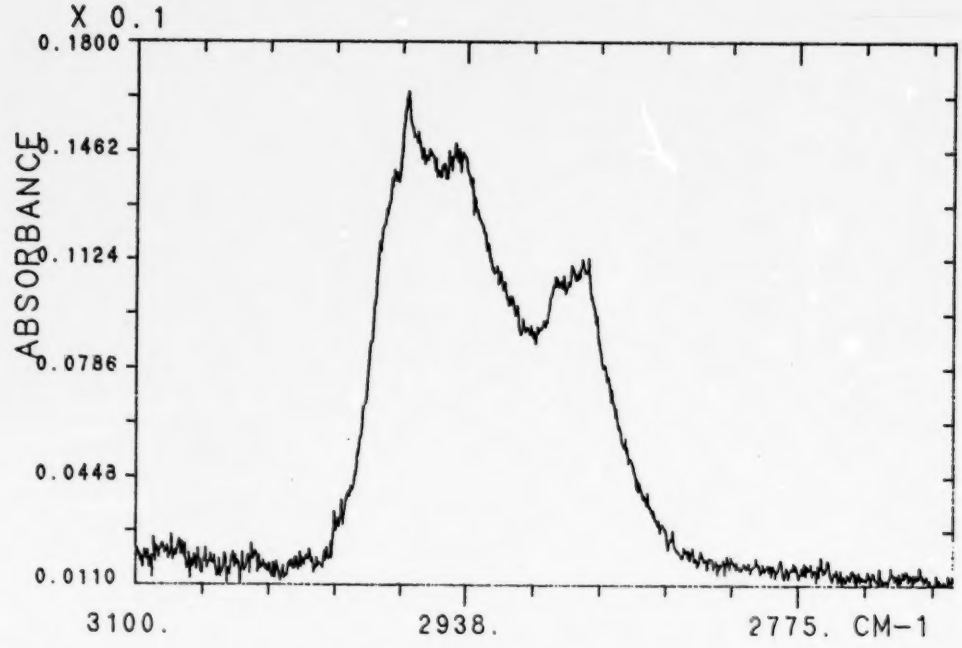

Figure C-21. Calibration of spectrometer for n-butanol at .1024 torr. Source 25 cm from aperture and 16 cm cell 740.0 torr.

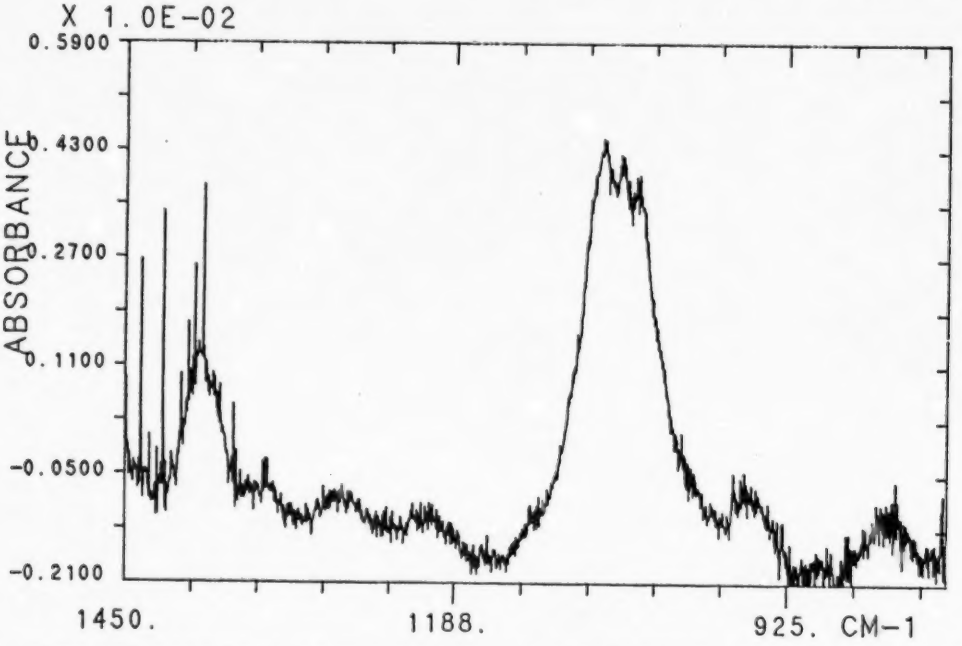

Figure C-22. Calibration of spectrometer for n-butanol at .1024 torr. Source 25 cm from aperture and 16 cm cell 740.0 torr.

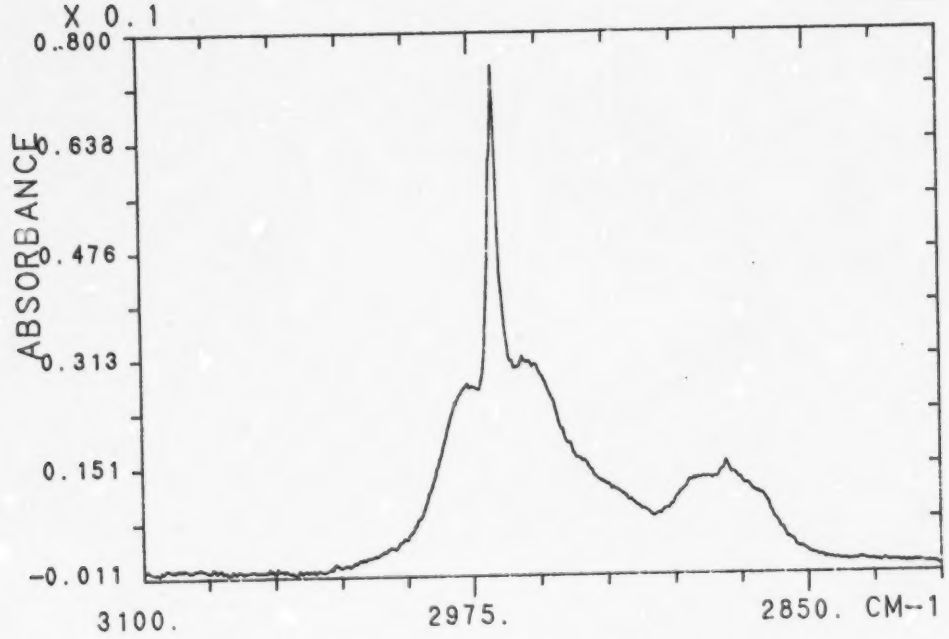

Figure C-23. Calibration of spectrometer for cyclopentane at .100 torr. Source 25 cm from aperture and 16 cm cell 740.1 torr.

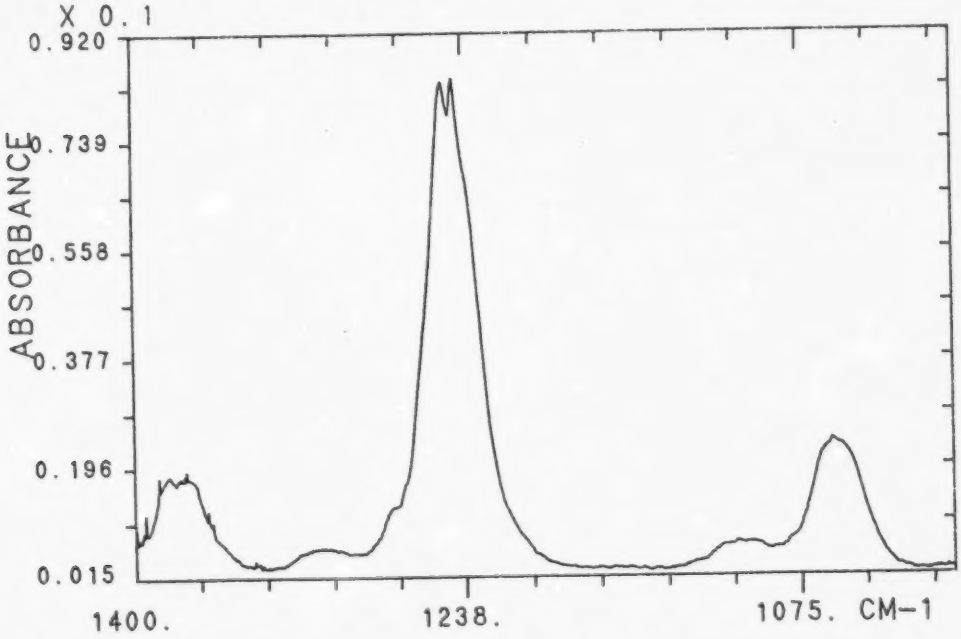

Figure C-24. Calibration of spectrometer for ethyl acetate at .1160 torr. Source 25 cm from aperture and 16 cm cell 740.0 torr.

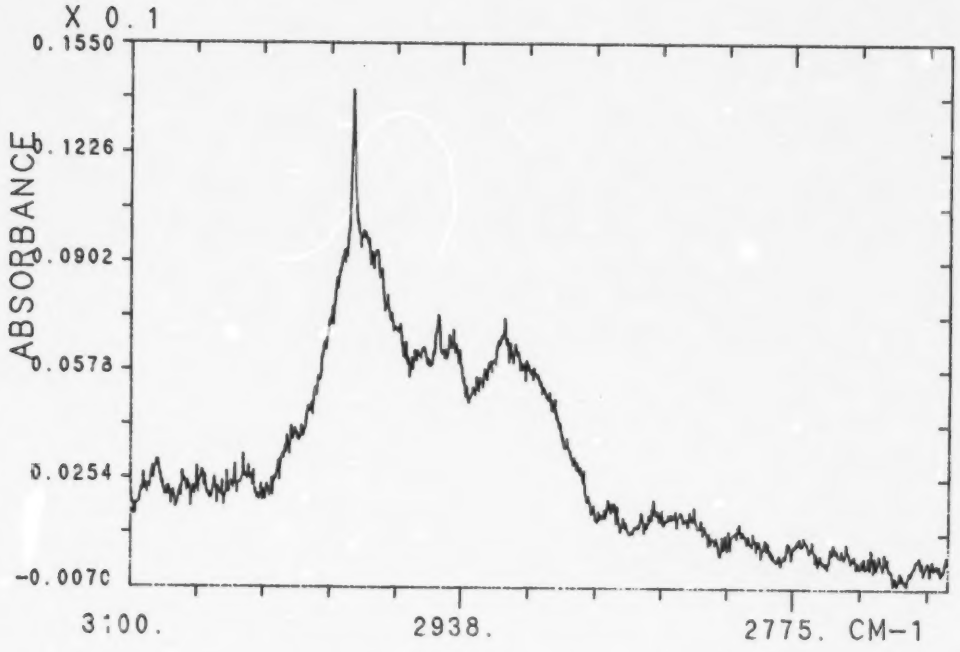

Figure C-25. Calibration of spectrometer for methyl ethyl ketone at .1234 torr. Source 25 cm from aperture and 16 cm cell 740.0 torr.

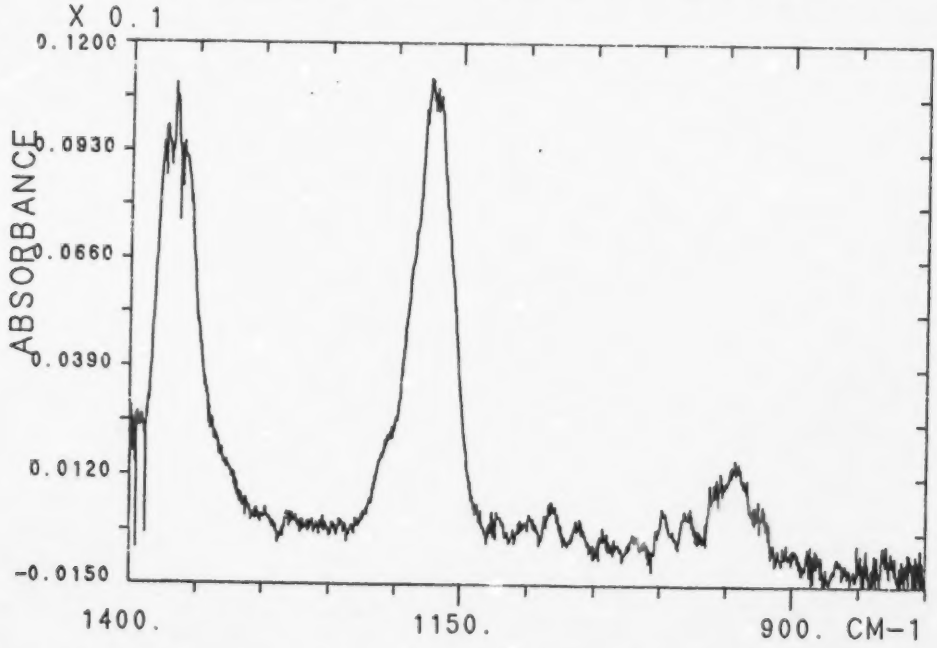

Figure C-26. Calibration of spectrometer for methyl ethyl ketone at .1234 torr. Source 25 cm from aperture and 16 cm cell 740.0 torr.

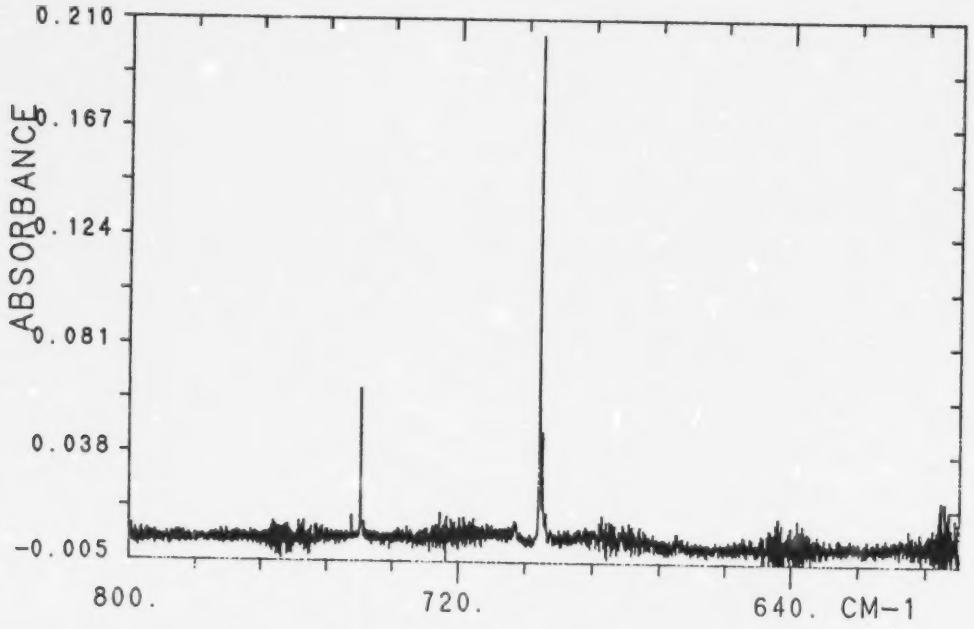

Figure C-27. Calibration of spectrometer for pyridine at .0973 torr. Source 25 cm from aperture and 16 cm cell 740.1 torr.

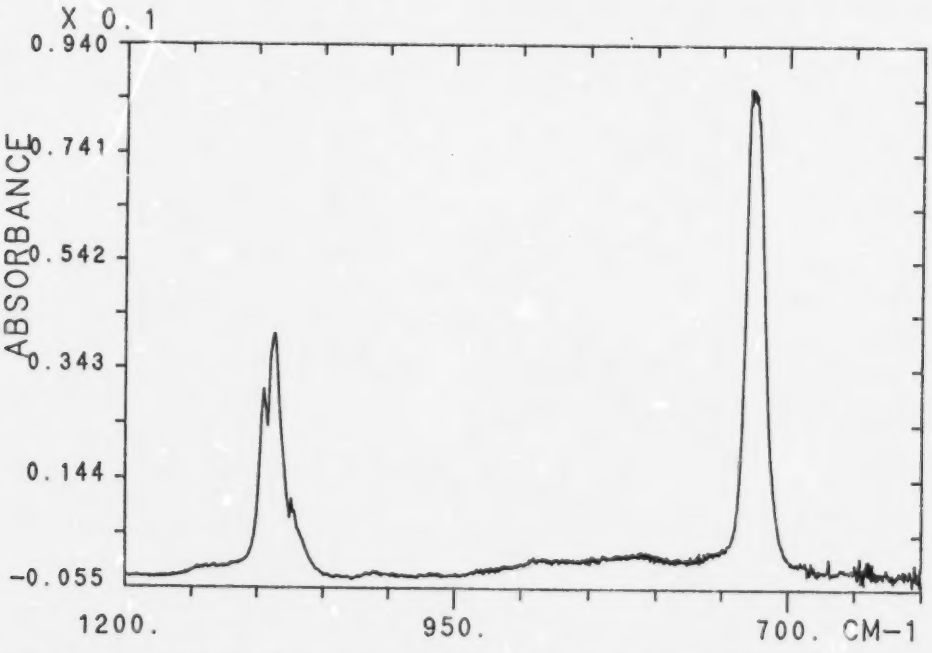

Figure C-28. Calibration of spectrometer for 1,1,1-trichloroethane at .1530 torr. Source 25 cm from aperture and 16 cm cell 740.0 torr.

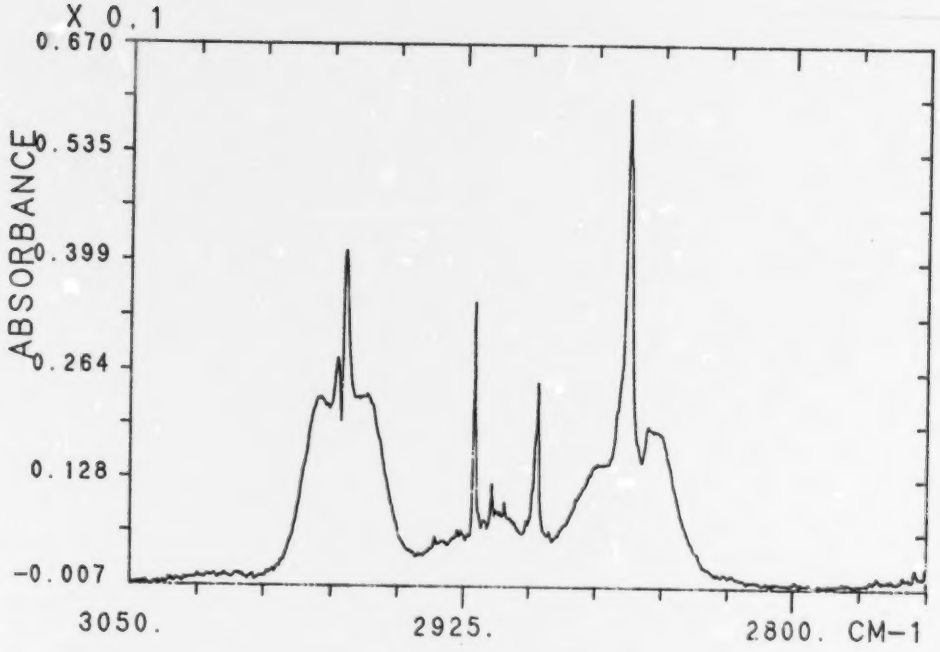

Figure C-29. Calibration of spectrometer for 1,4-dioxane at .1086 torr. Source 25 cm from aperture and 16 cm cell 740.1 torr.

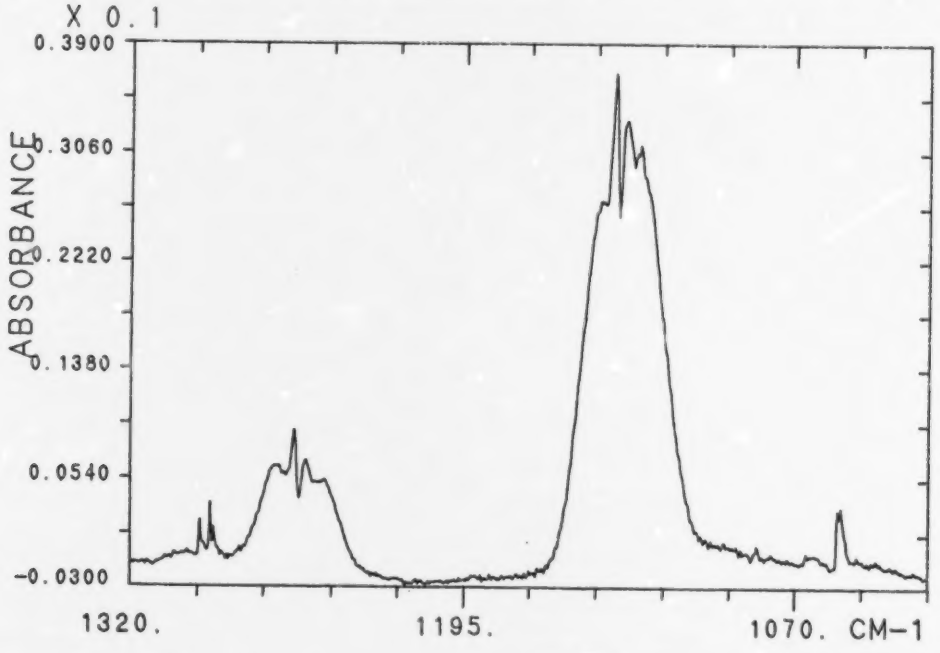

Figure C-30. Calibration of spectrometer for 1,4-dioxane at .1086 torr. Source 25 cm from aperture and 16 cm cell 740.1 torr.

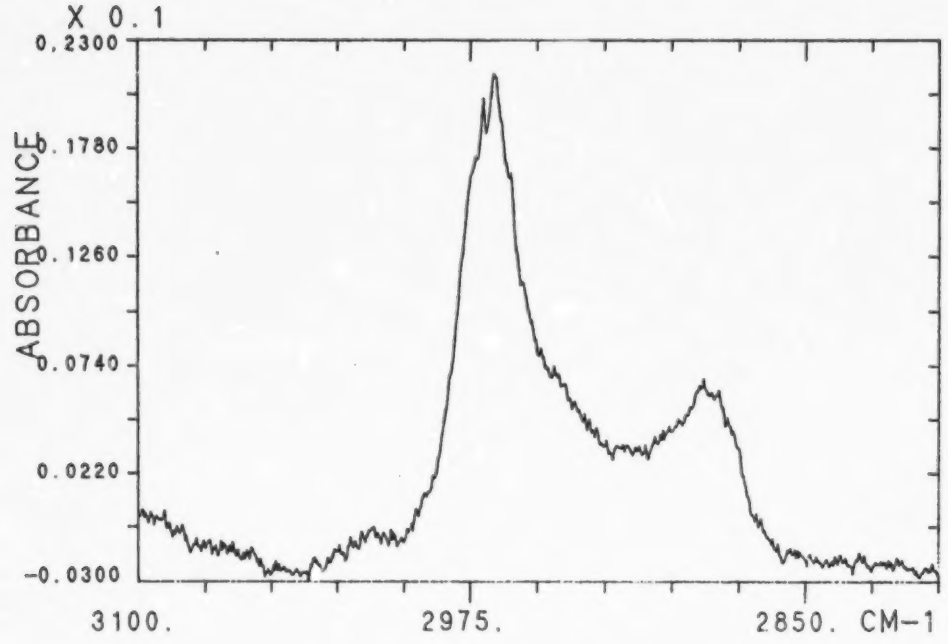

Figure C-31. Calibration of spectrometer for methyl isobutyl ketone at .1124 torr. Source 25 cm from aperture and 16 cm cell 740.1 torr.

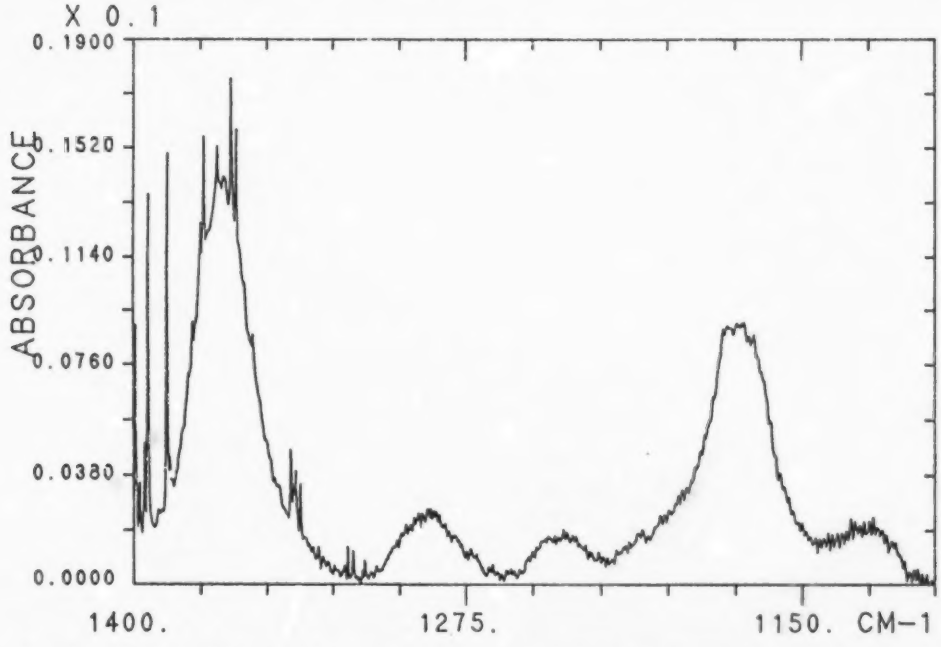

Figure C-32. Calibration of spectrometer for methyl isobutyl ketone at .1124 torr. Source 25 cm from aperture and 16 cm cell 740.1 torr.

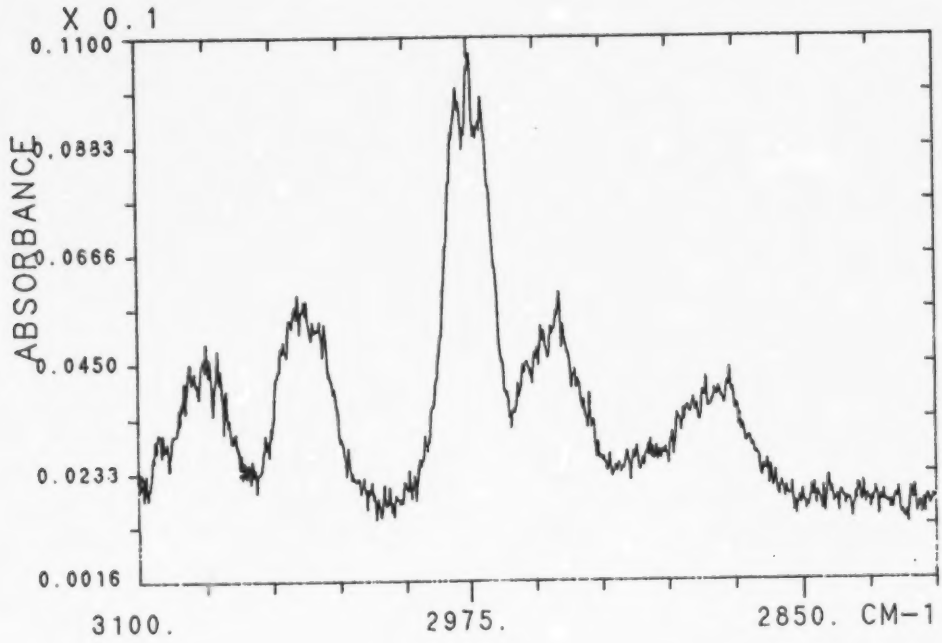

Figure C-33. Calibration of spectrometer for ethyl benzene at .0724 torr. Source 25 cm from aperture and 16 cm cell 740.0 torr.

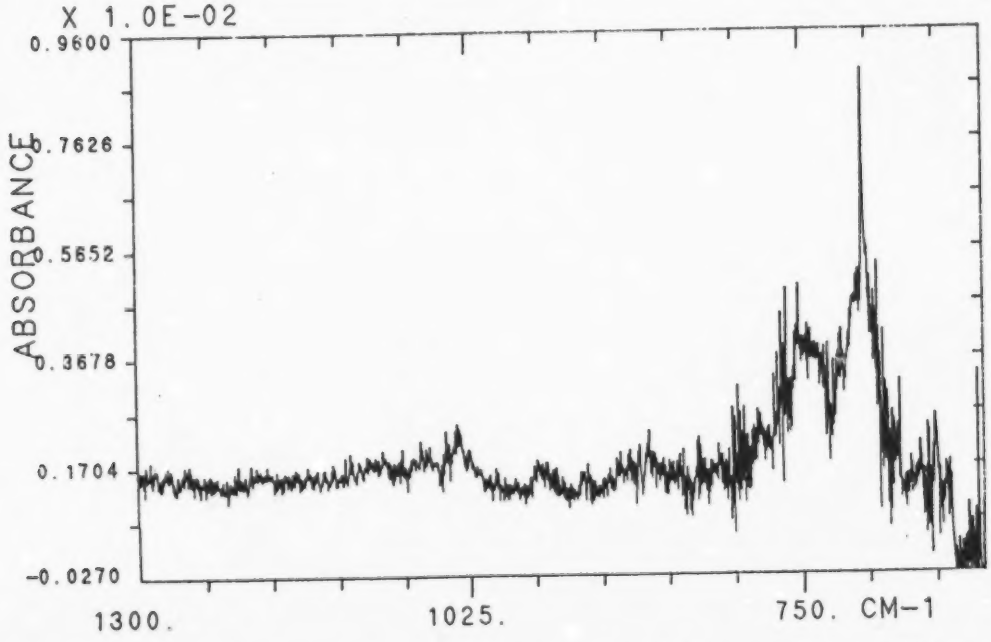

Figure C-34. Calibration of spectrometer for ethyl benzene at .0724 torr. Source 25 cm from aperture and 16 cm cell 740.0 torr.

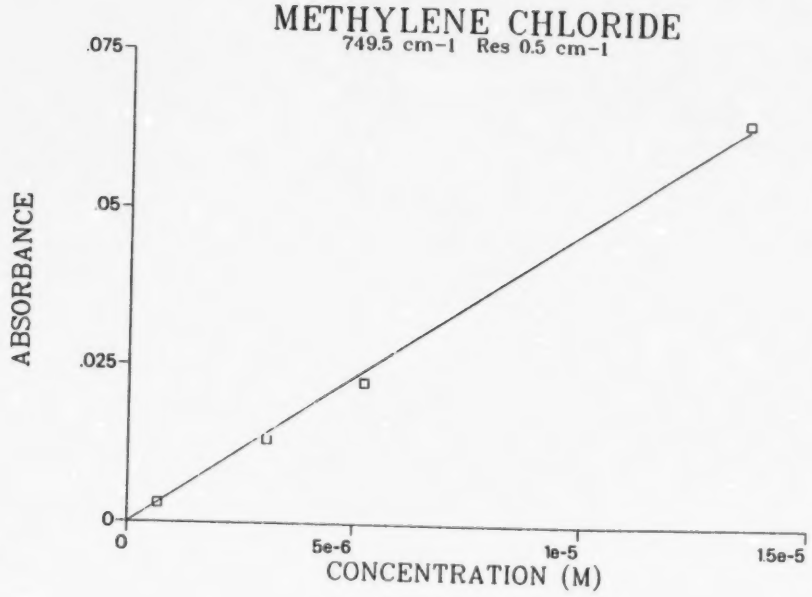

Figure C-35. Methylene chloride.

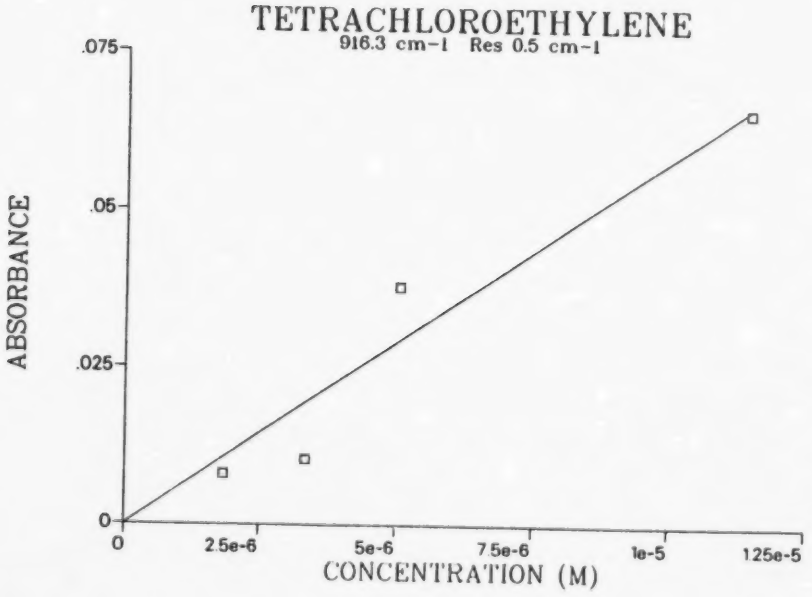

Figure C-36. Tetrachloroethylene.

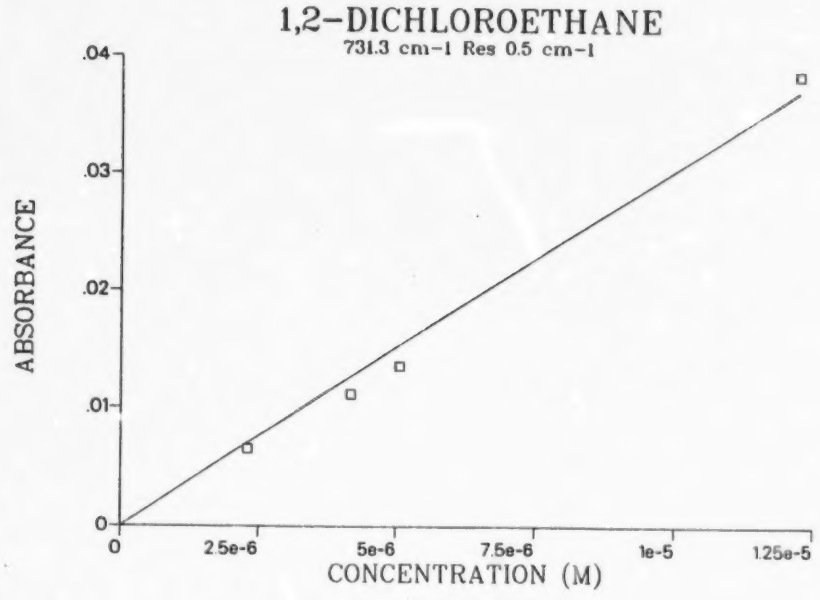

Figure C-37. 1,2-Dichloroethane.

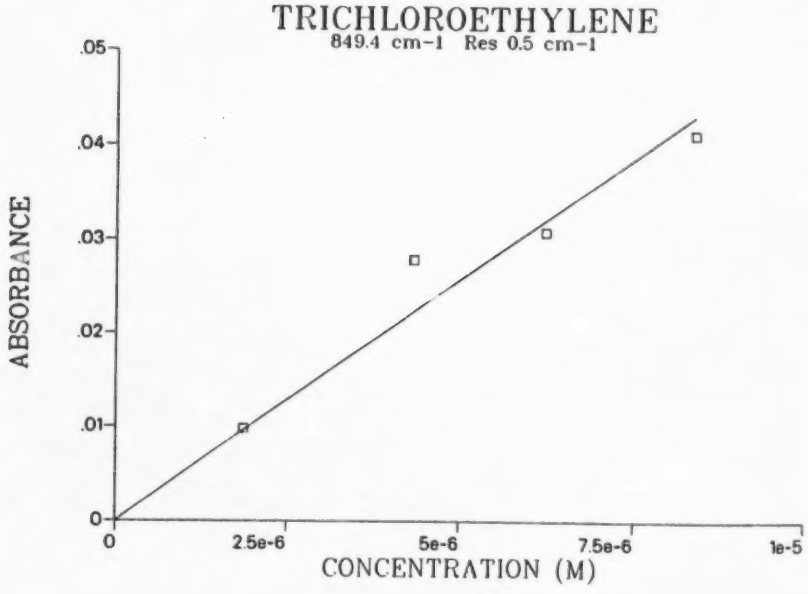

Figure C-38. Trichloroethylene.

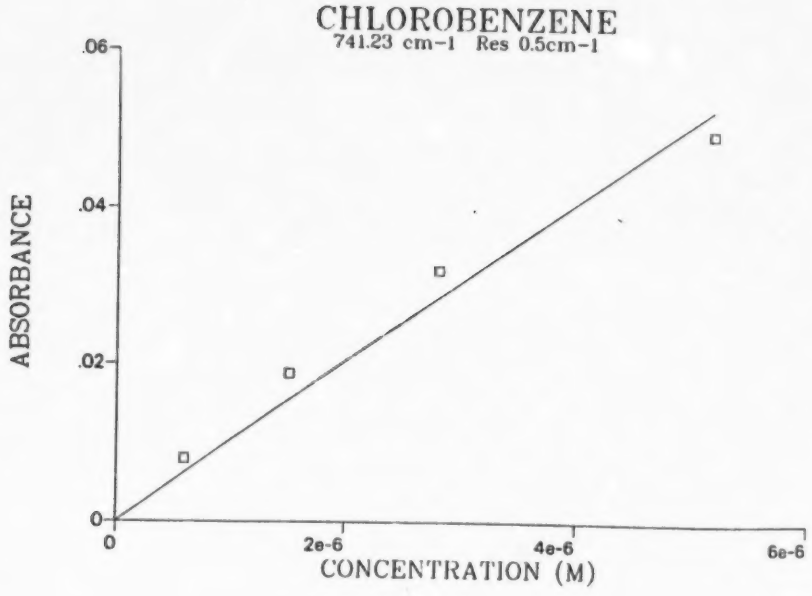

Figure C-39. Chlorobenzene.

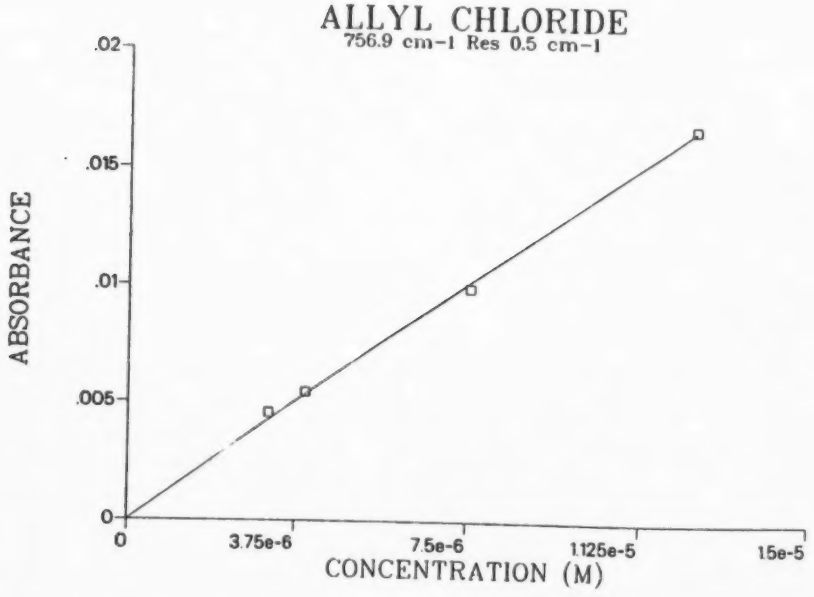

Figure C-40. Allyl chloride (3-Chloropropene).

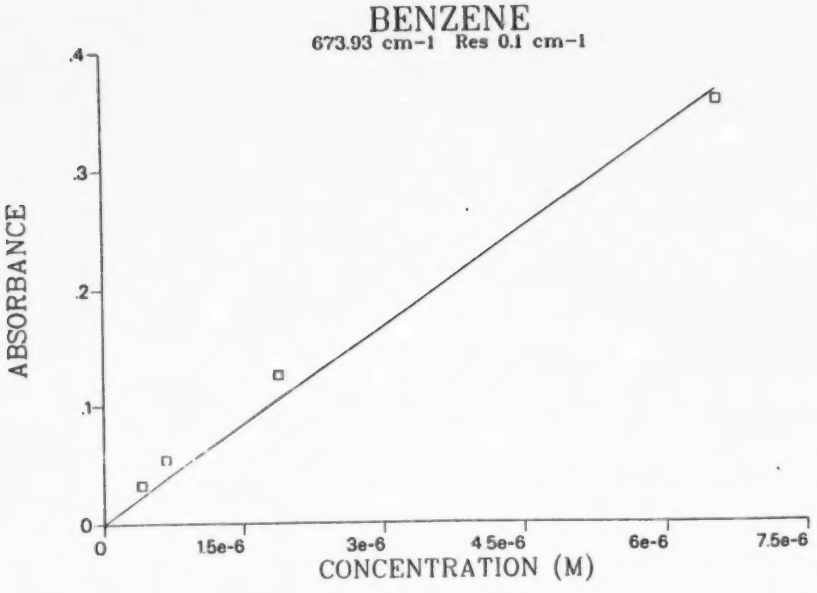

Figure C-41. Benzene.

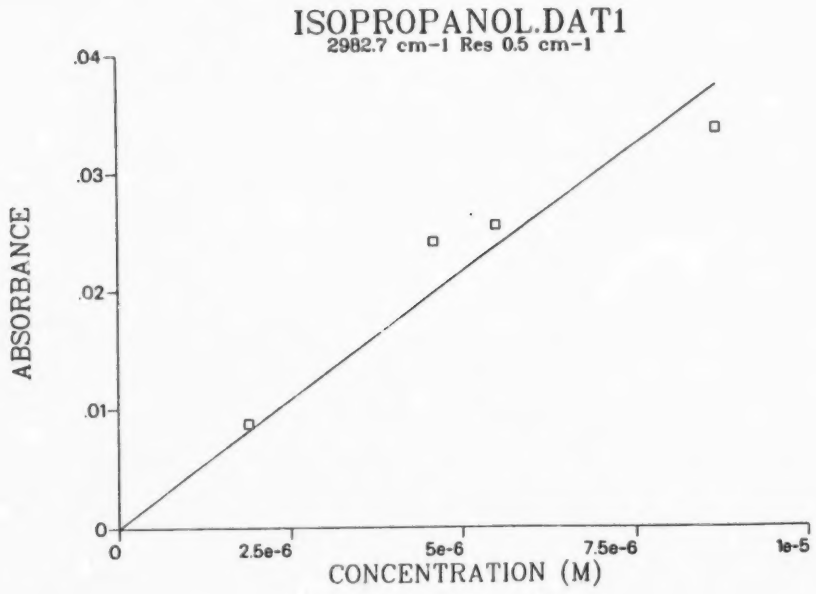

Figure C-42. Isopropanol.Dat 1.

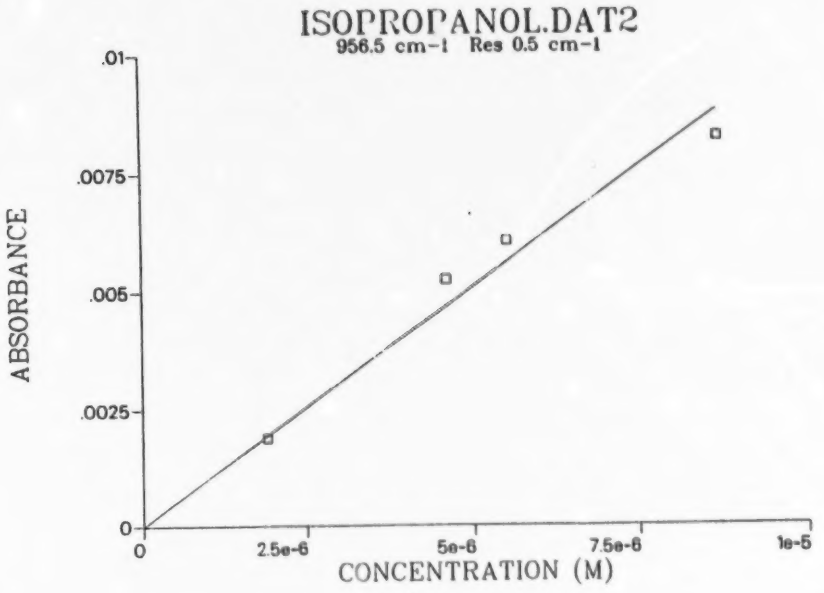

Figure C-43. Isopropanol.Dat 2.

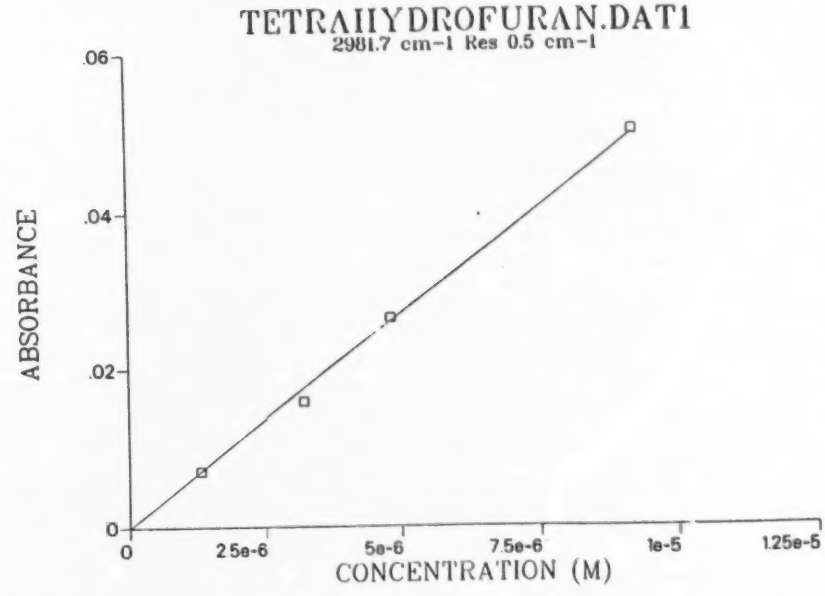

Figure C-44. Tetrahydrofuran.Dat 1.

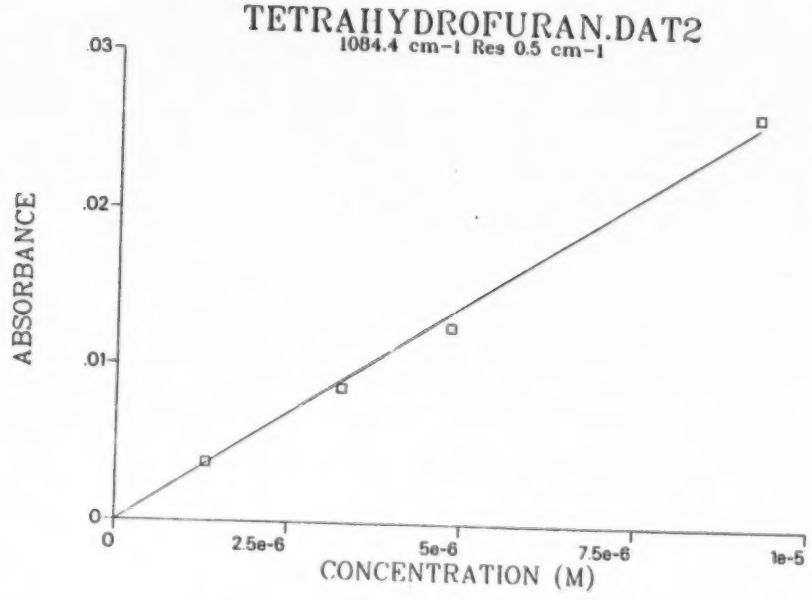

Figure C-45. Tetrahydrofuran.Dat 2.

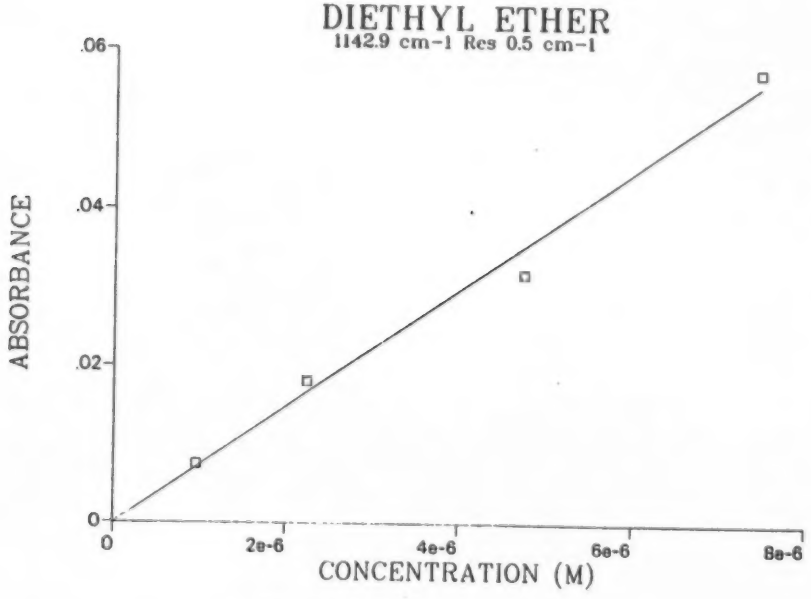

Figure C-46. Diethyl ether.

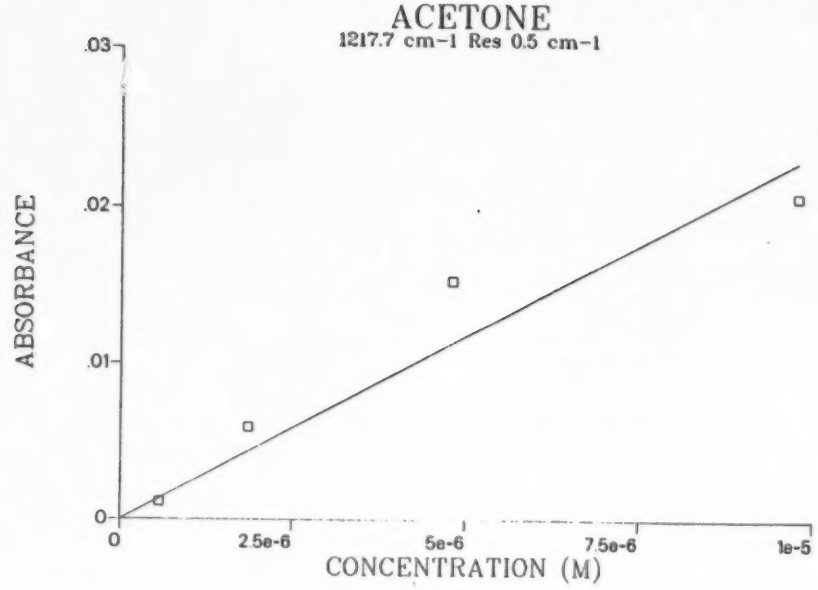

Figure C-47. Acetone.

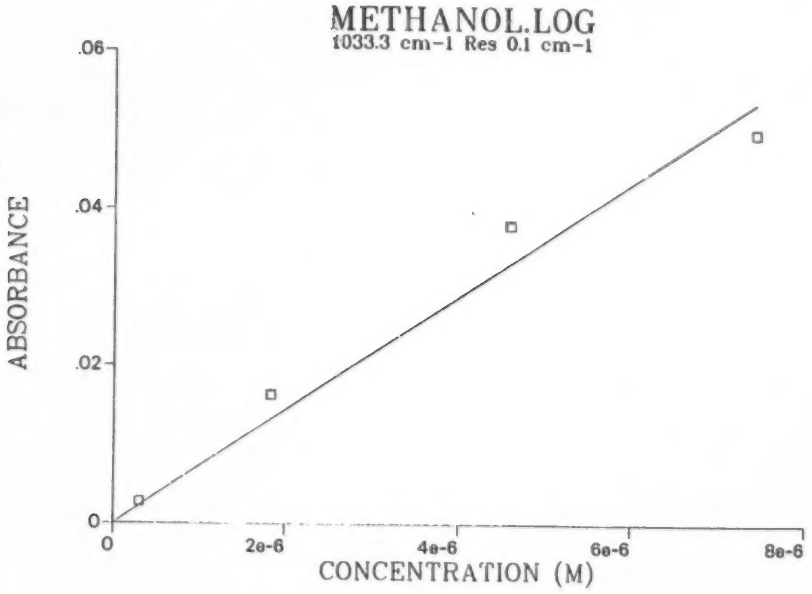

Figure C-48. Methanol.Log.

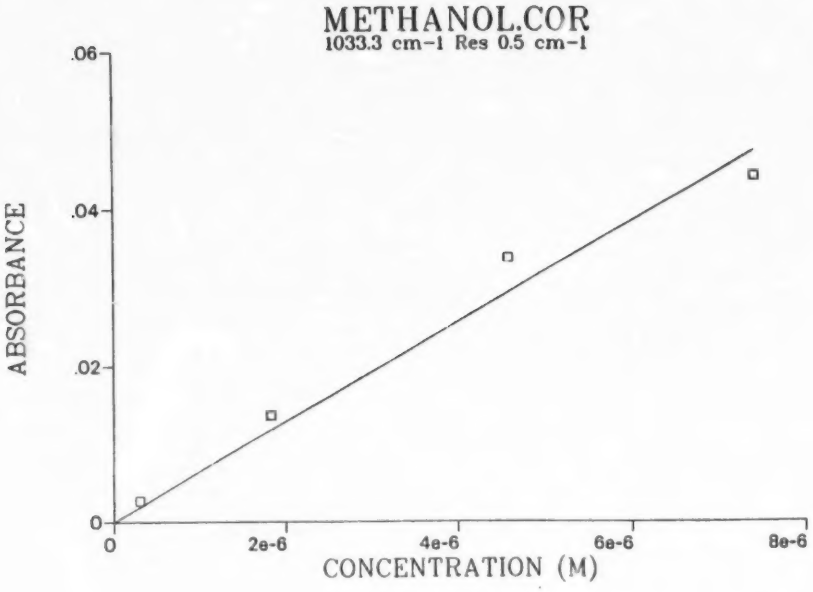

Figure C-49. Methanol.Cor.

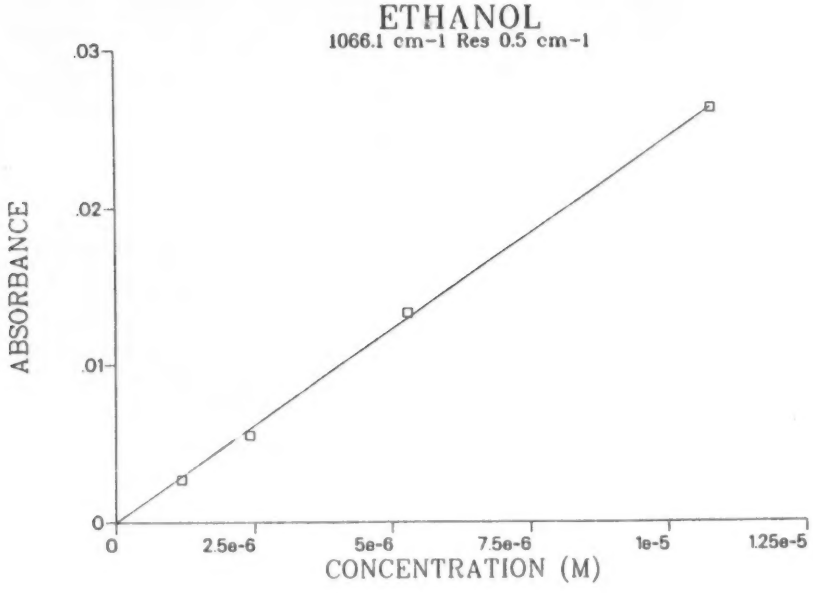

Figure C-50. Ethanol.

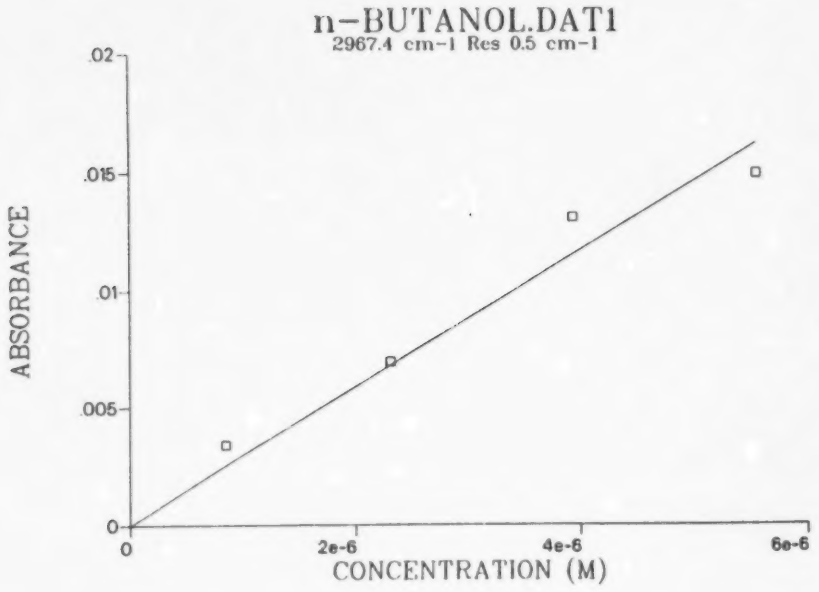

Figure C-51. n-Butanol.Dat 1.

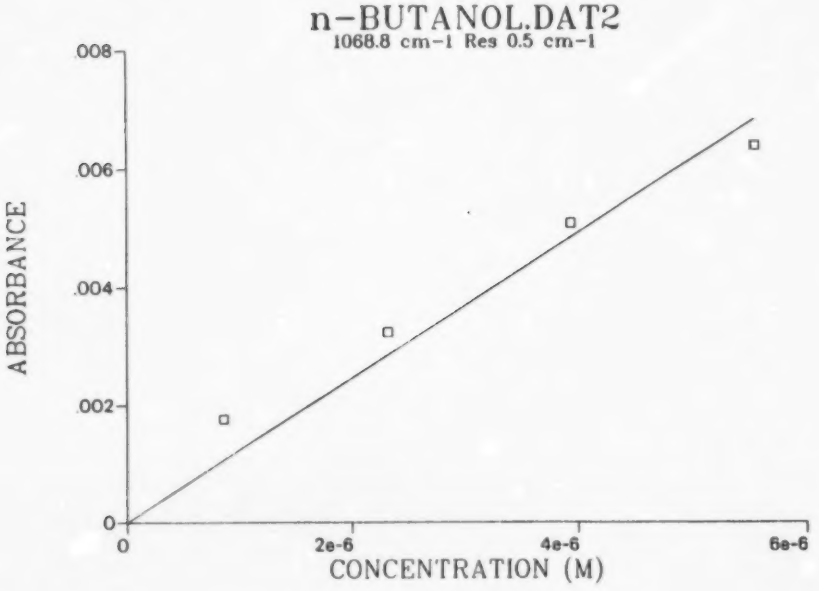

Figure C-52. n-Butanol.Dat 2.

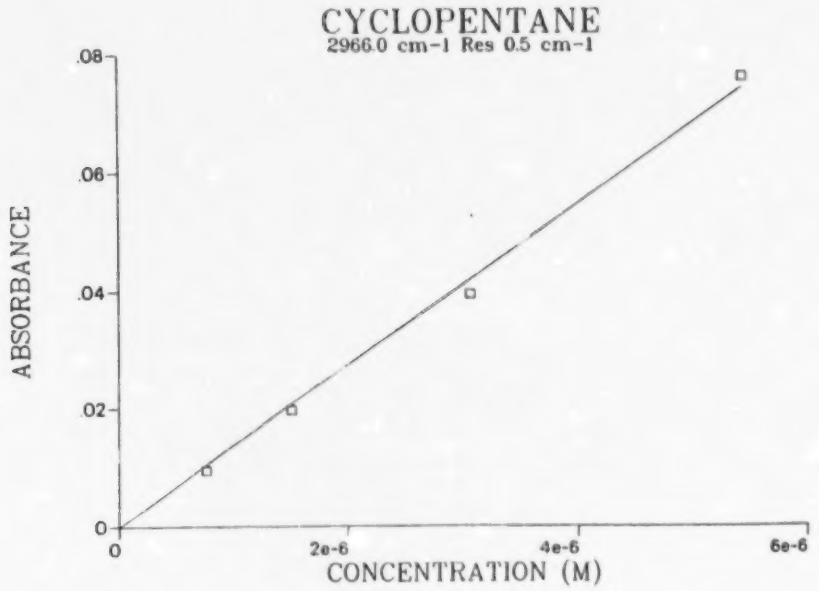

Figure C-53. Cyclopentane.

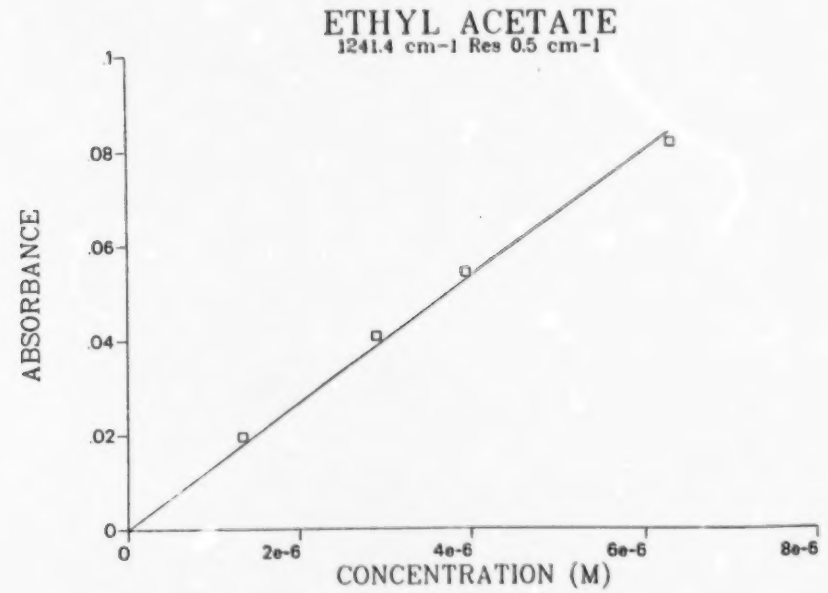

Figure C-54. Ethyl acetate.

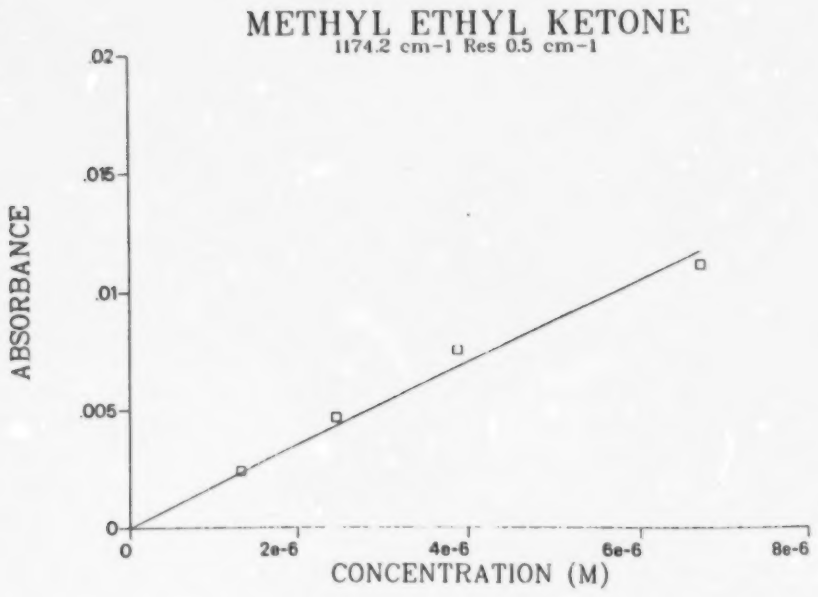

Figure C-55. Methyl ethyl ketone.

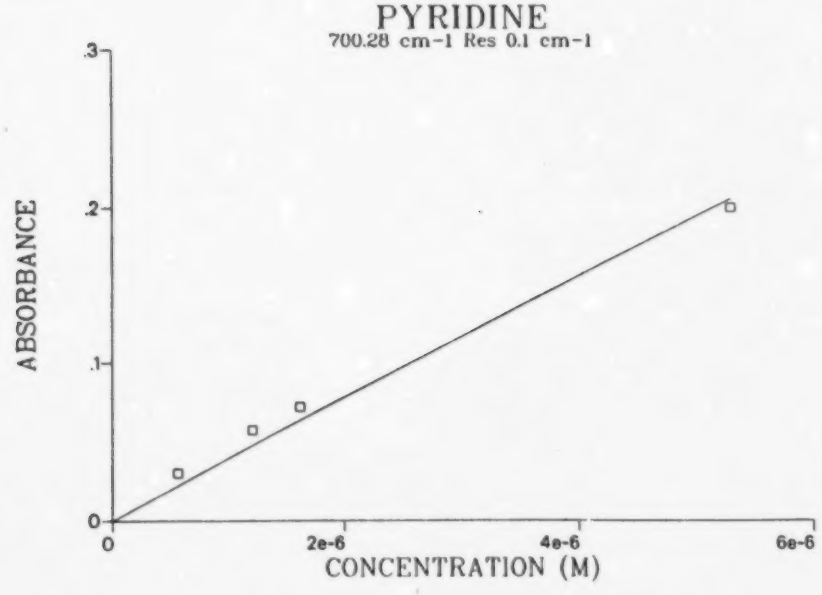

Figure C-56. Pyridine.

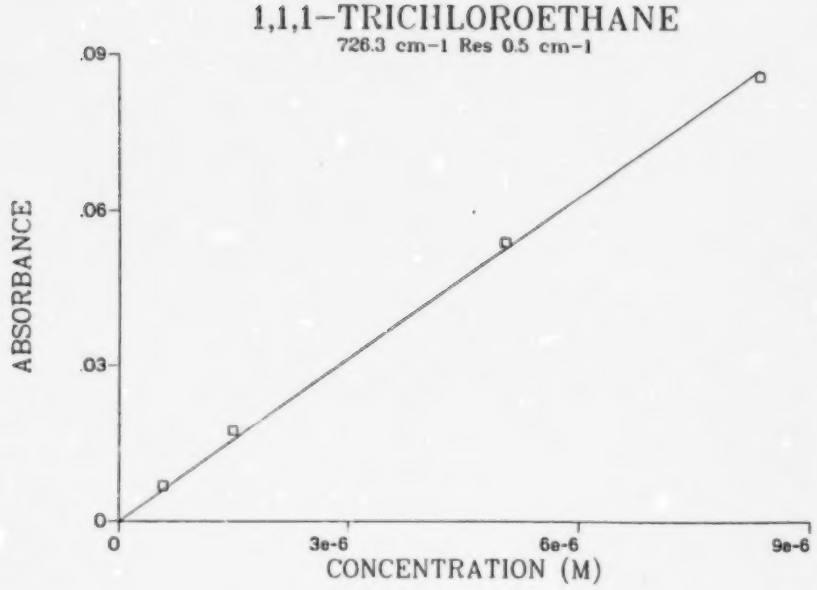

Figure C-57. 1,1,1-Trichloroethane (1,1,1-TCA).

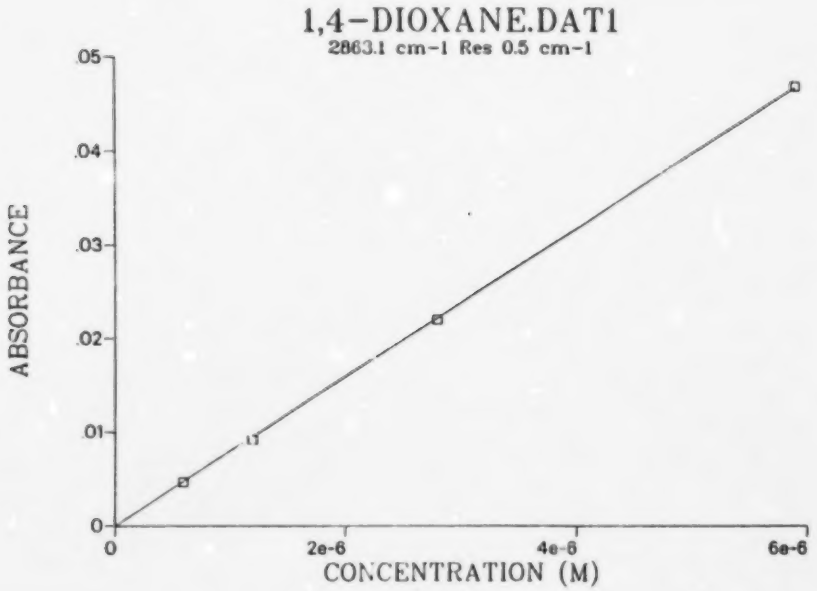

Figure C-58. 1,4 Dioxane.Dat 1.

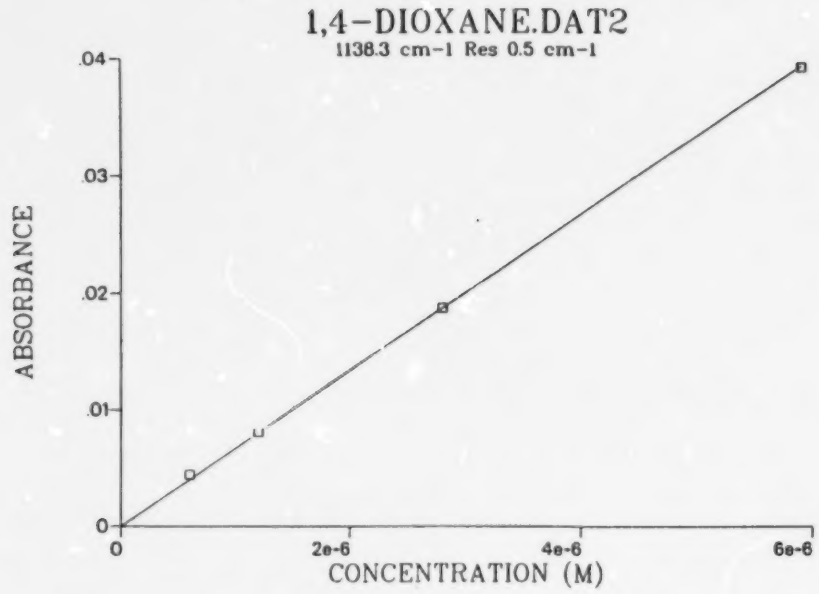

Figure C-59. 1,4-Dioxane.Dat 2.

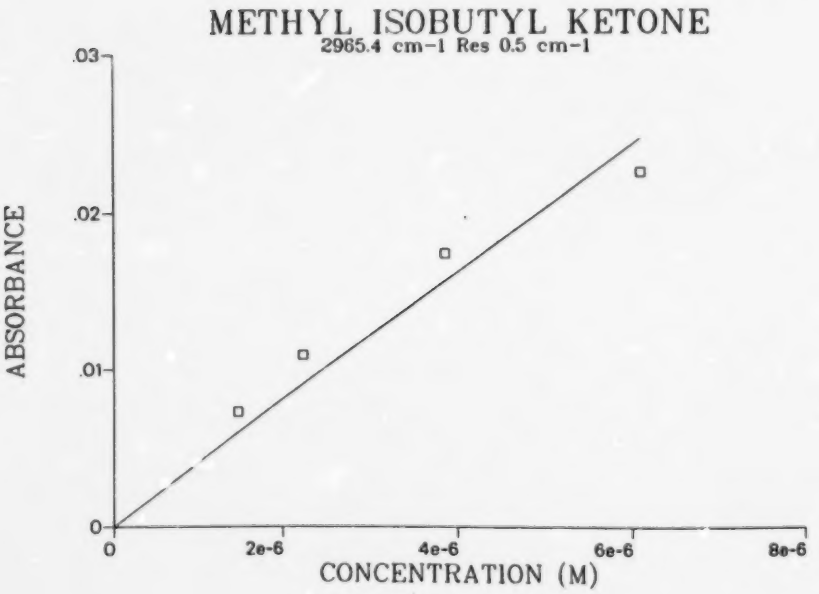

Figure C-60. Methyl isobutyl ketone.

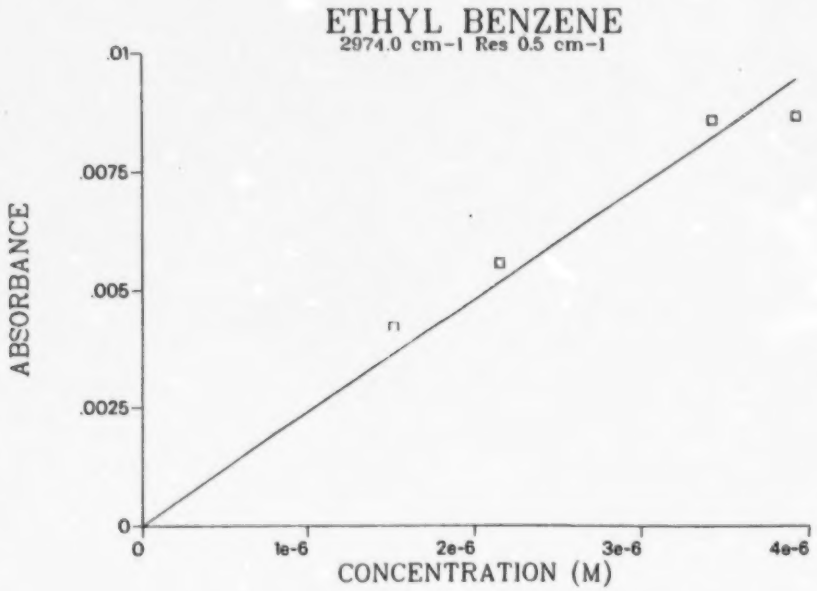

Figure C-61. Ethylbenzene.

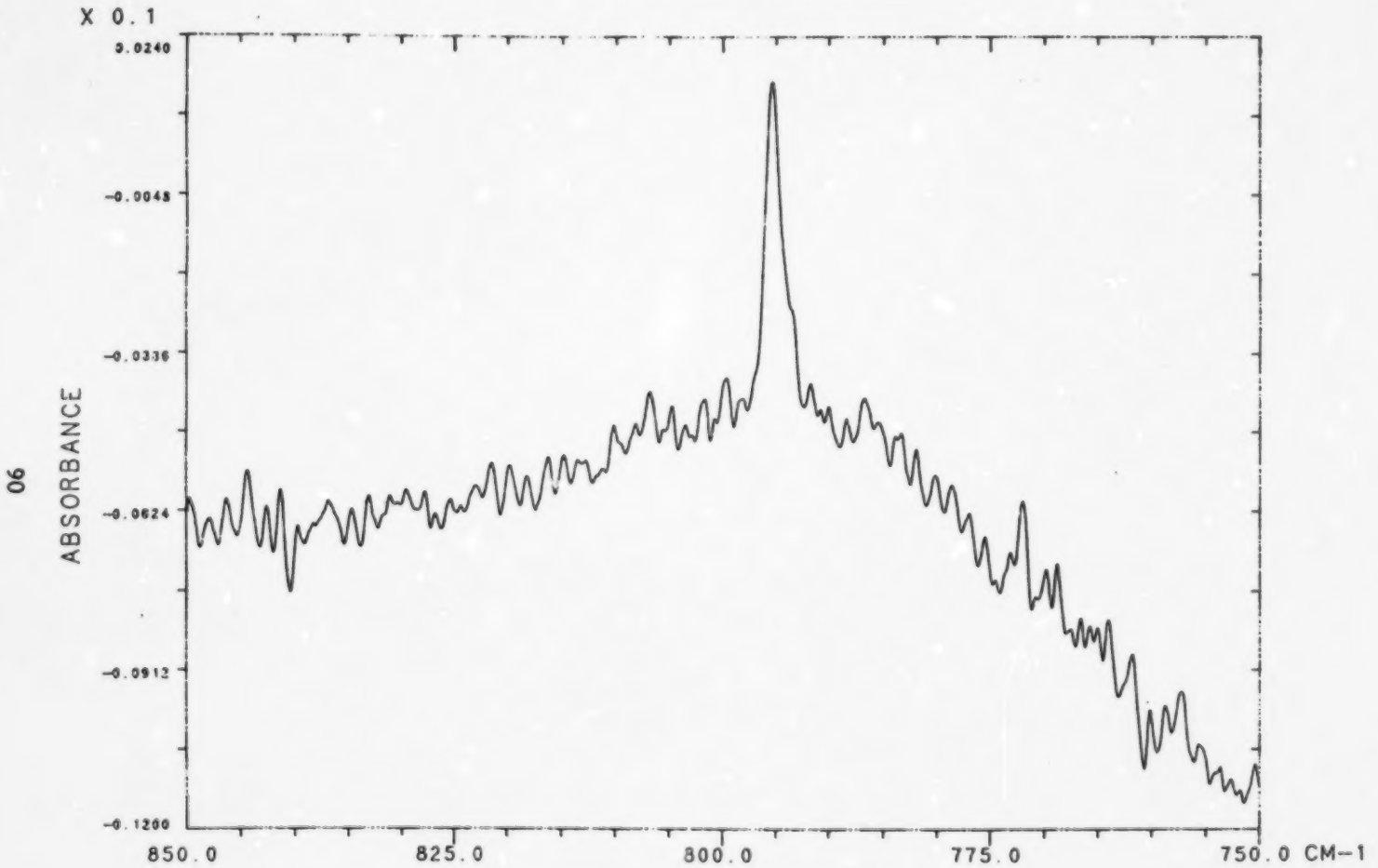

Figure C-62. Calibration of spectrometer for p-xylene at 0.0462 torr. Source 25 cm from aperture and 16 cm cell mirror 35 cm 740.3 torr.

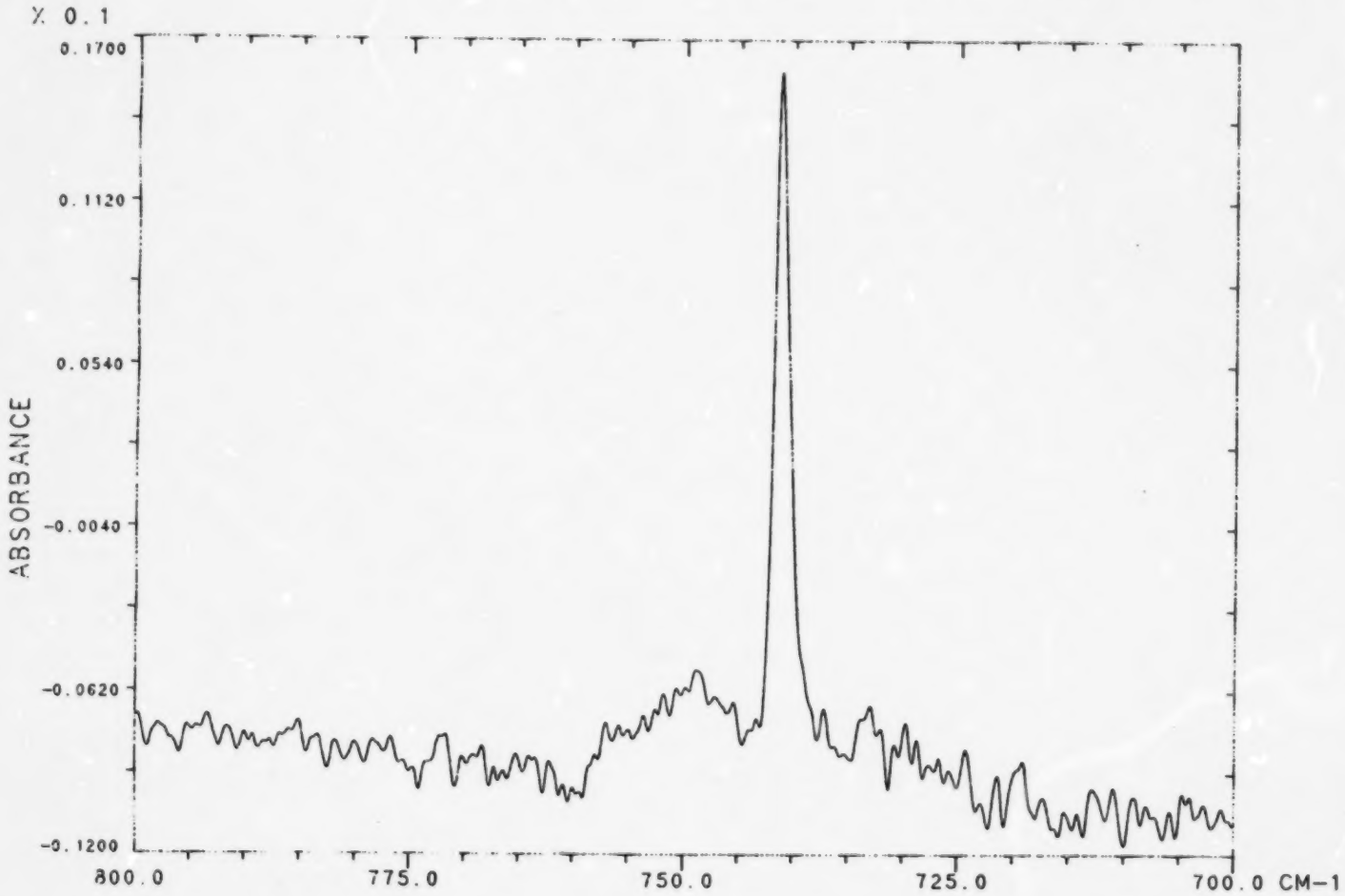

Figure C-63. Calibration of spectrometer for o-xylene at 0.0687 torr. Source 25 cm from aperture and 16 cm cell mirror 35 cm 740.0 torr.

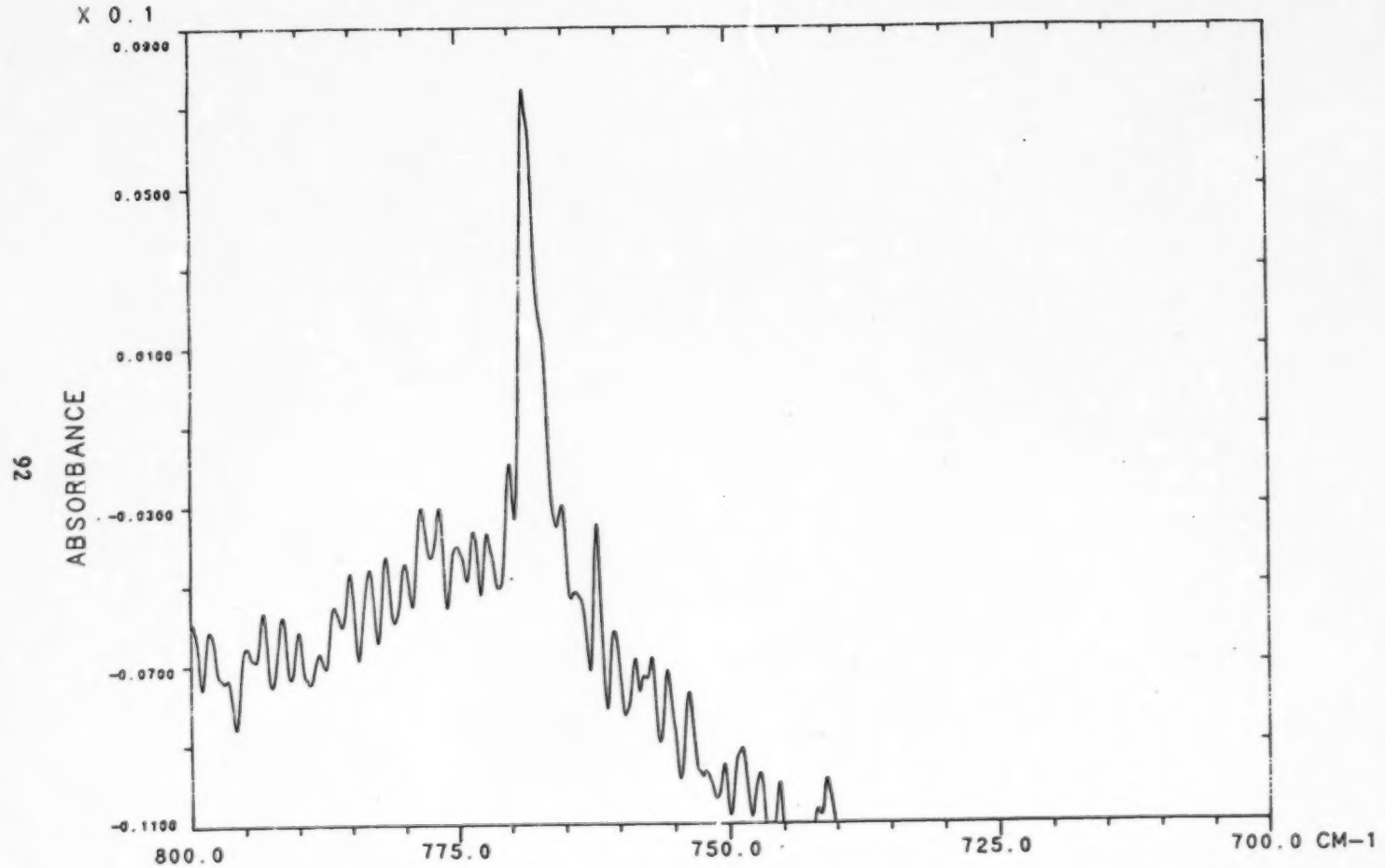

Figure C-64. Calibration of spectrometer for m-xylene at 0.0868 torr. Source 25 cm from aperture and 16 cm cell mirror 35 cm 740.0 torr.

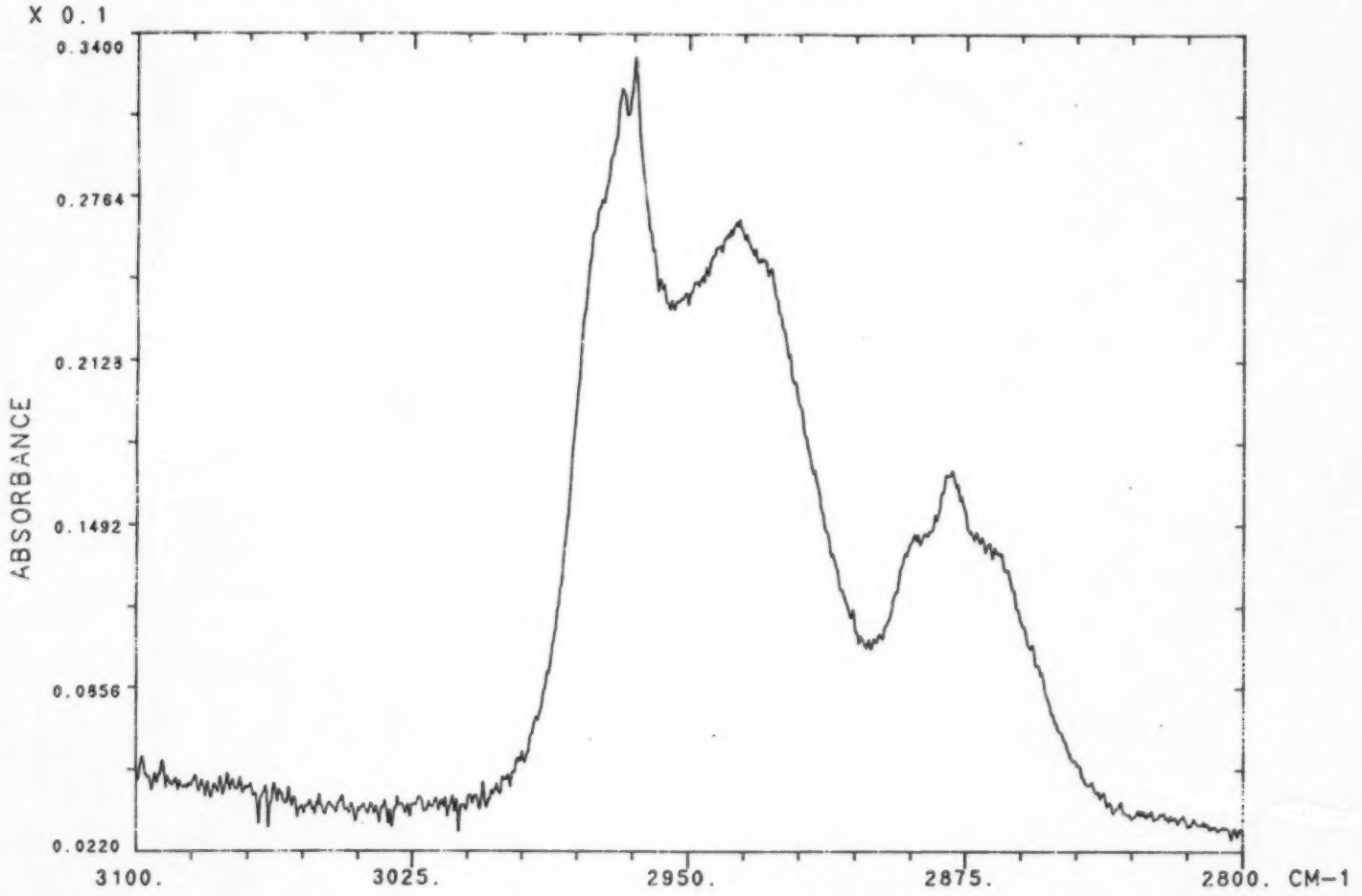

Figure C-65. Calibration of spectrometer for n-hexane at 0.0844 torr. Source 25 cm from aperture and 16 cm cell mirror 35 cm 740.4 torr.

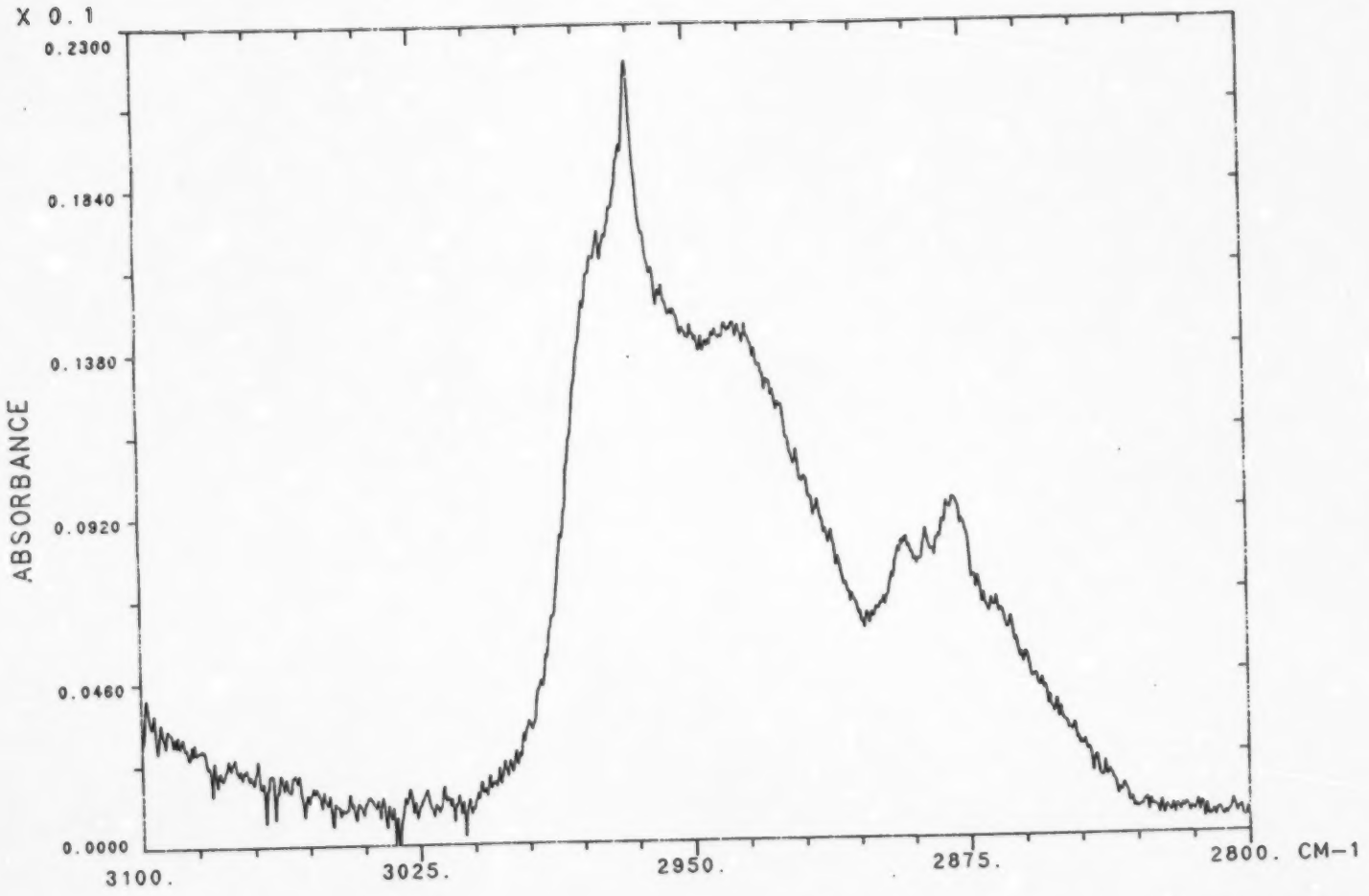

Figure C-66. Calibration of spectrometer for n-pentane at 0.0788 torr. Source 25 cm from aperture and 16 cm cell mirror 35 cm 740.0 torr.

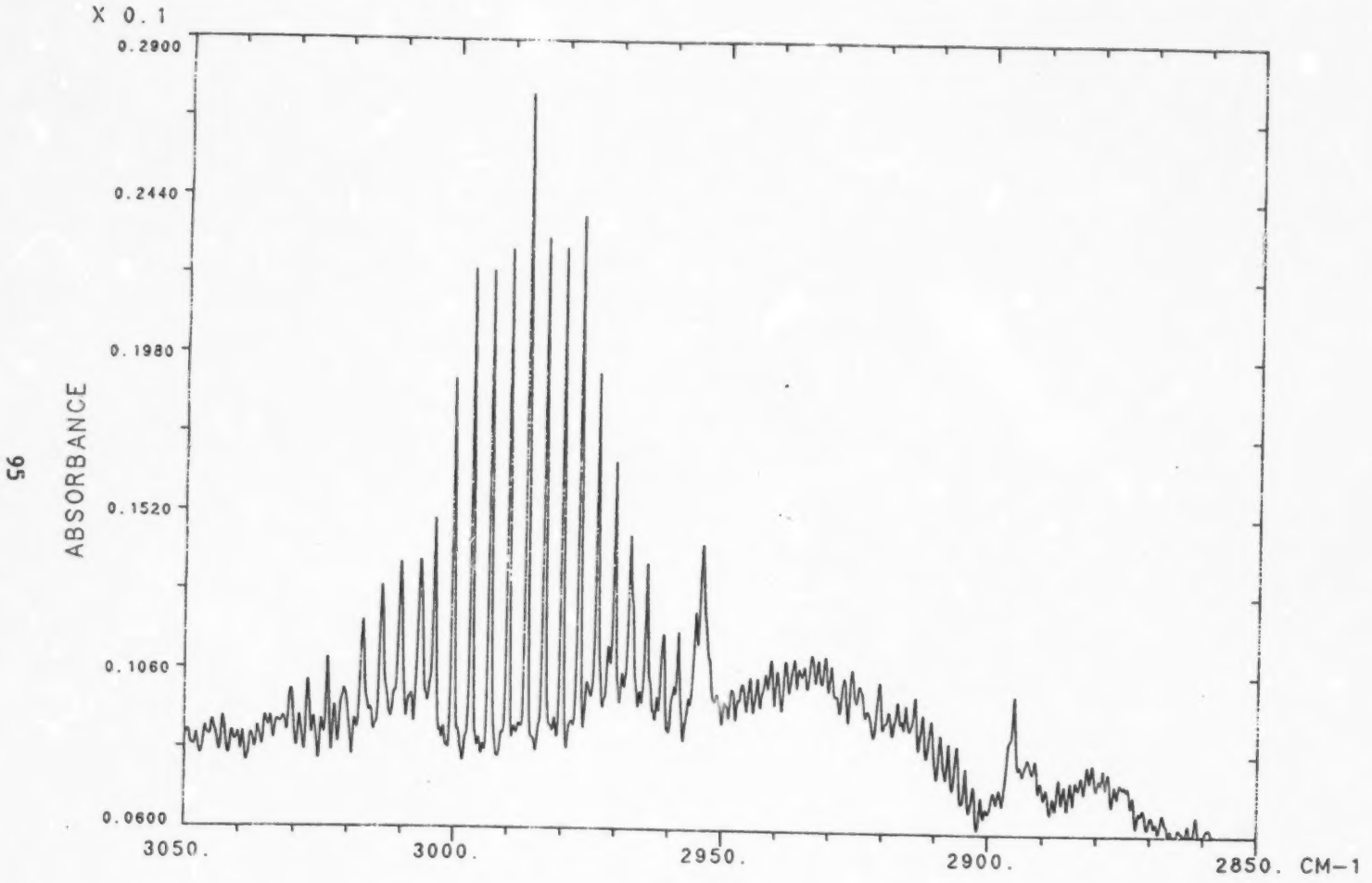

Figure C-67. Calibration of spectrometer for ethane at .0649t ? Lect. bottles. Source 25 cm from aperture and 16 cm cell mirror 35 cm 740.0 torr.

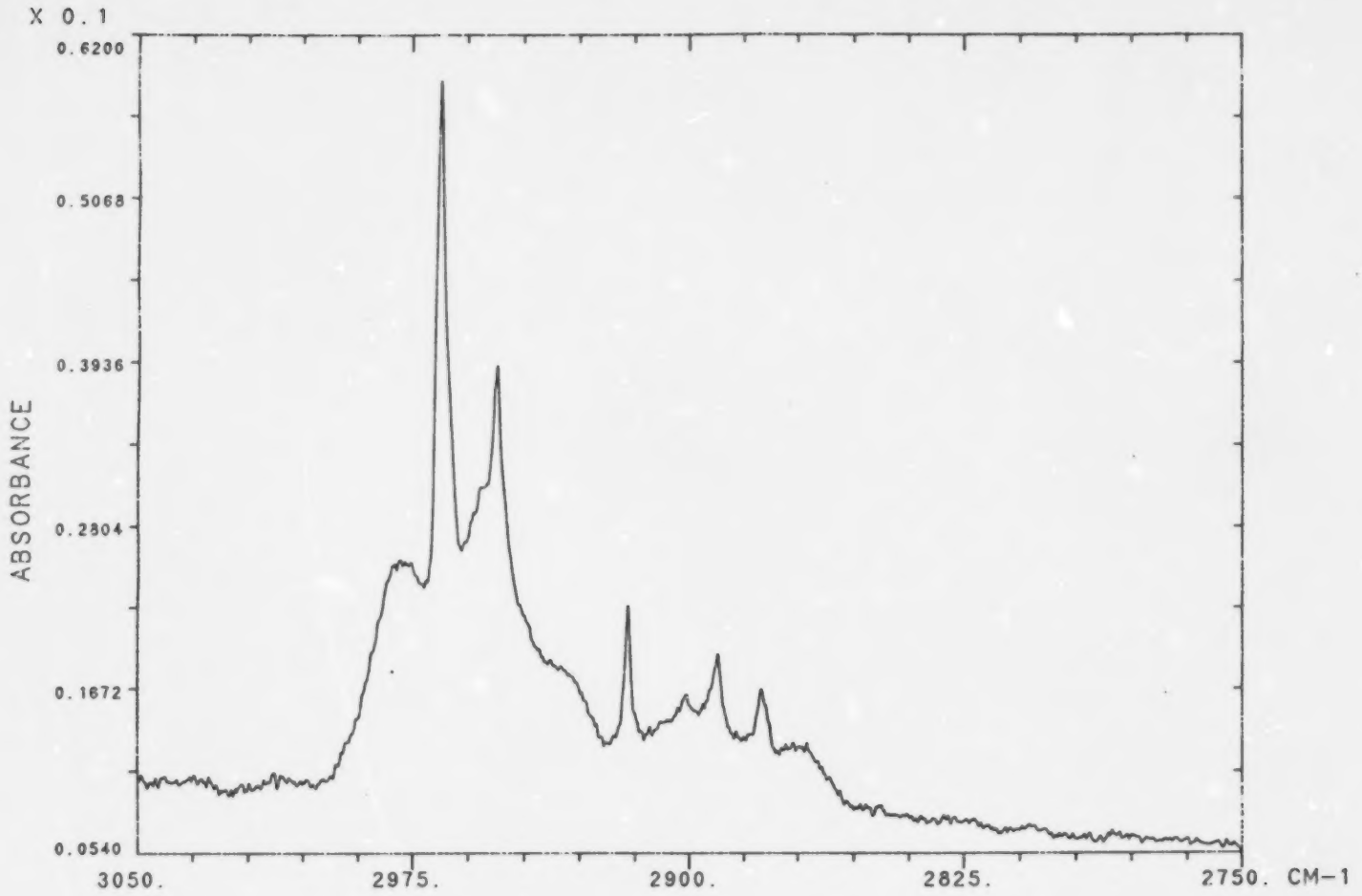

Figure C-68. Calibration of spectrometer for isobutane at .0746t ? Lect. bottles. Source 25 cm from aperture and 16 cm cell mirror 35 cm 740.0 torr.

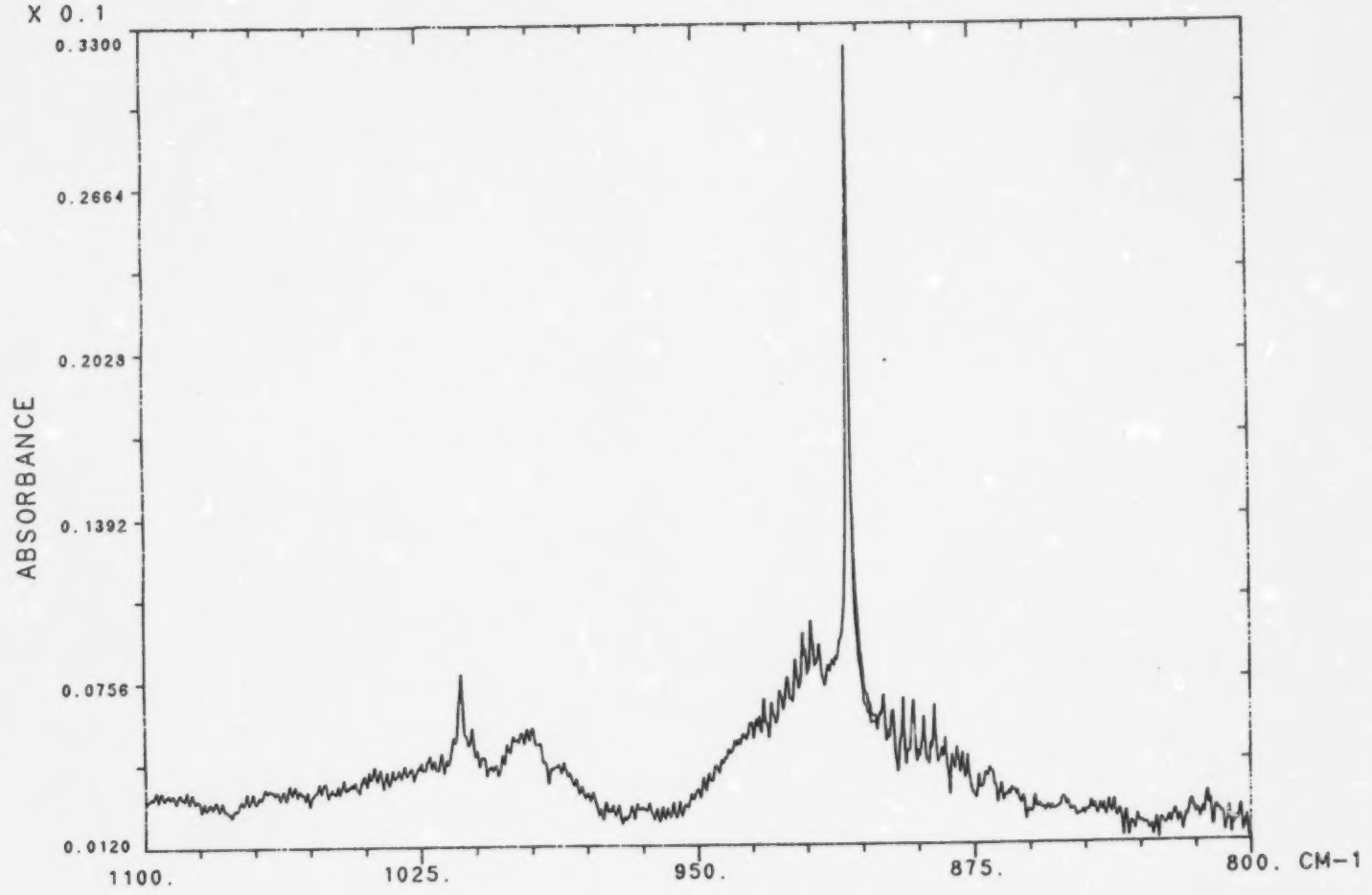

Figure C-69. Calibration of spectrometer for 1,3-butadiene at .0910t lec. bot. Source 25 cm from aperture and 16 cm cell mirror 35 cm 740.0 torr.

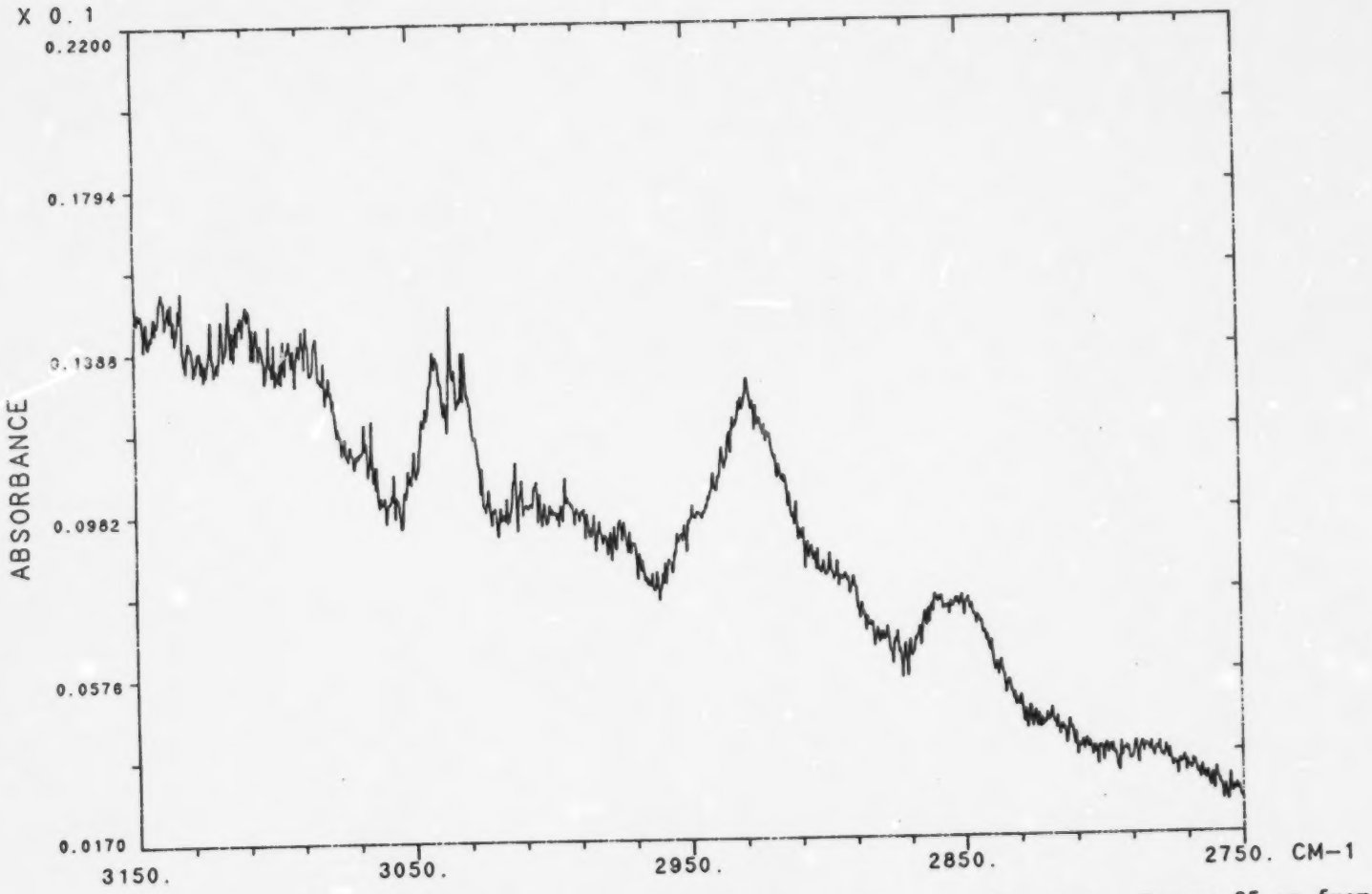

Figure C-70. Calibration of spectrometer for 1,3-butadiene at .0910 torr lec. bot. Source 25 cm from aperture and 16 cm cell mirror 35 cm 740.0 torr.

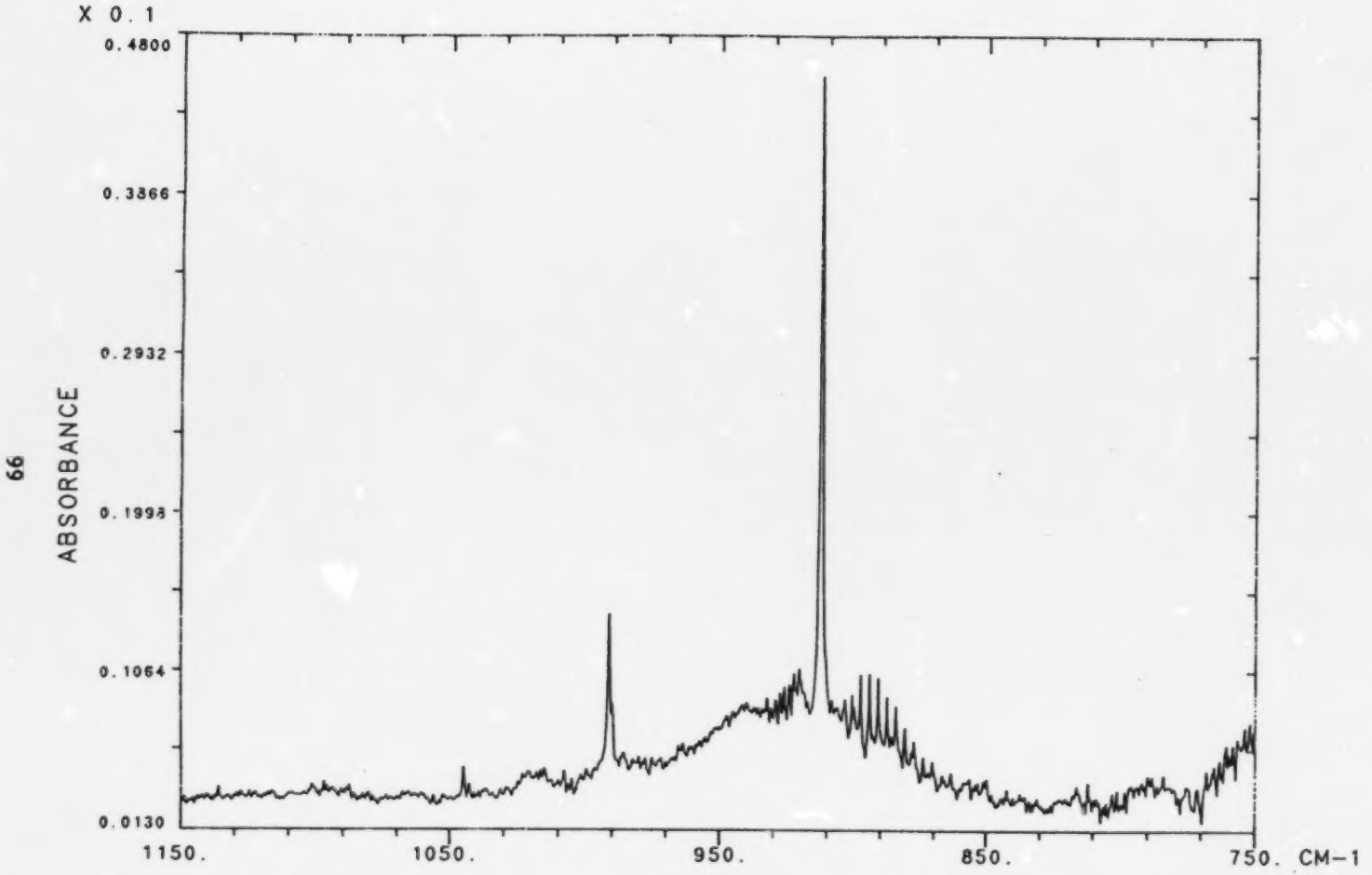

Figure C-71. Calibration of spectrometer for propylene at 0.1915 torr ? Lec. bot. Source 25 cm from aperture and 16 cm cell mirror 35 cm 740.0 torr.

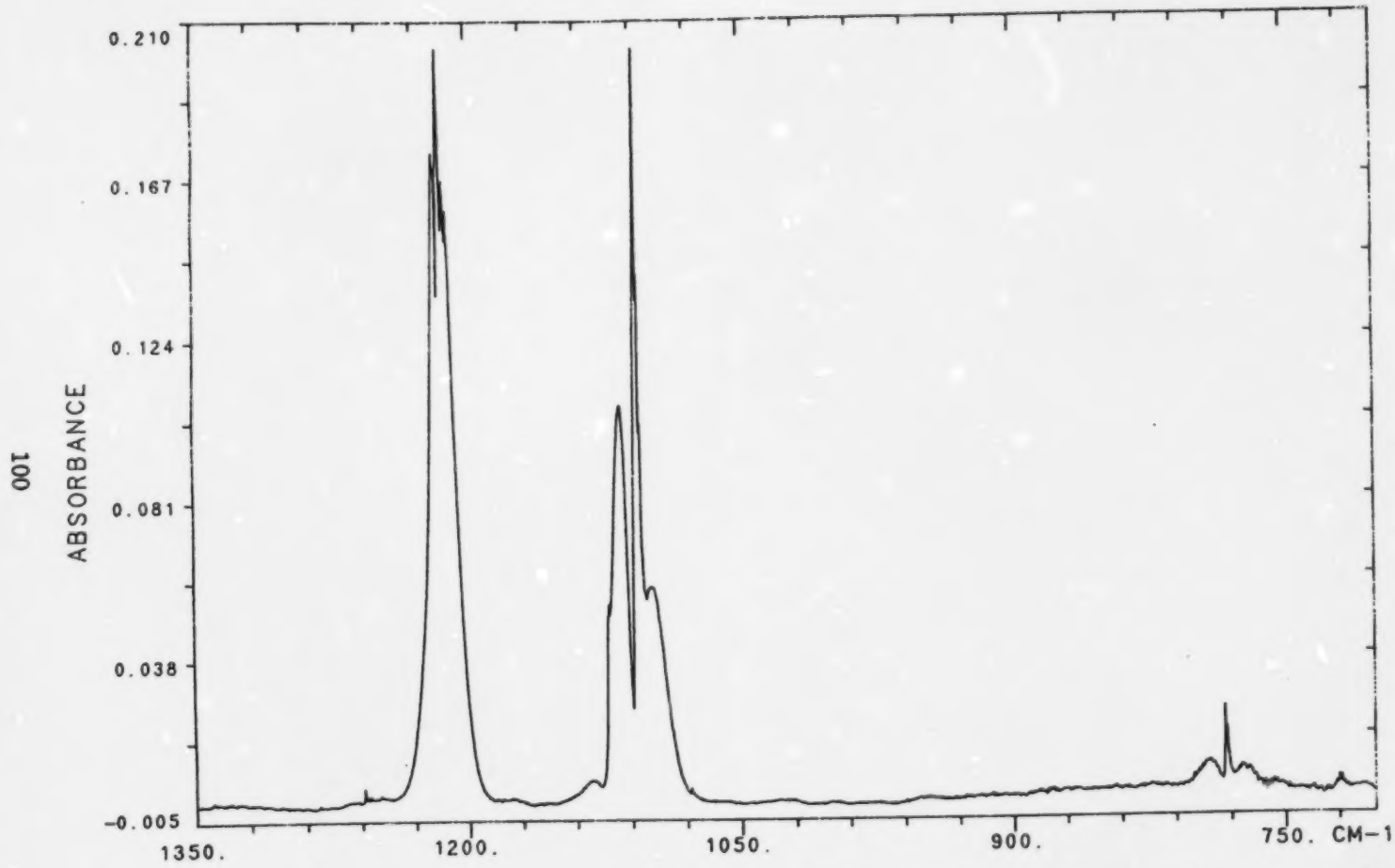

Figure C-72. Calibration of spectrometer for Freon 13 (CC1F3) at .1225 torr ? Lect. bot. Source 25 cm from aperture and 16 cm cell mirror 35 cm 740.0 torr.

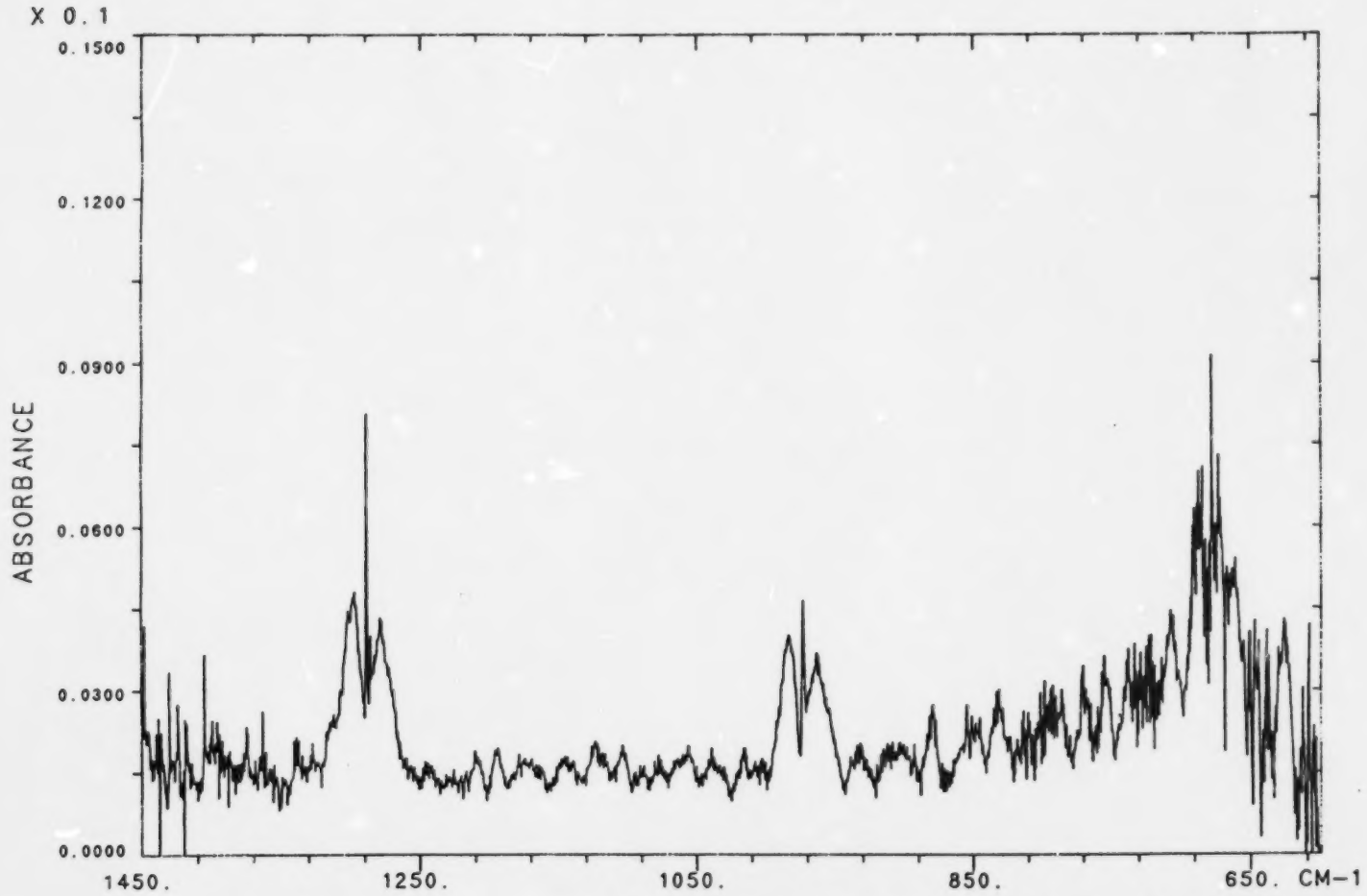

Figure C-73. Calibration of spectrometer for ethyl chloride at .1015 torr ? Lect. bot. Source 25 cm from aperture and 16 cm cell mirror 35 cm 740.1 torr.

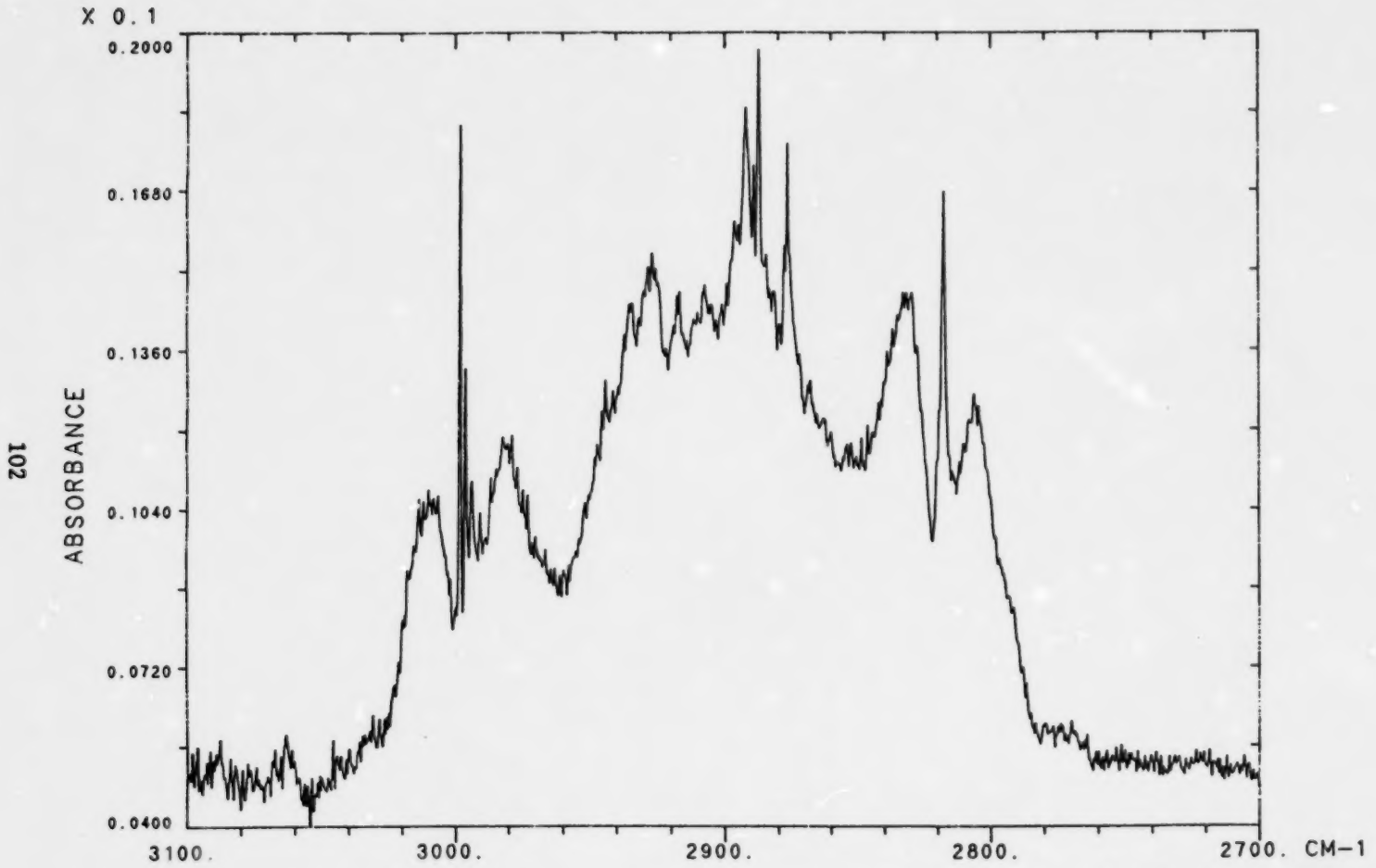

Figure C-74. Calibration of spectrometer for dimethyl ether at .1220 torr ? Lect. bot. Source 25 cm from aperture and 16 cm cell mirror 35 cm 740.0 torr.

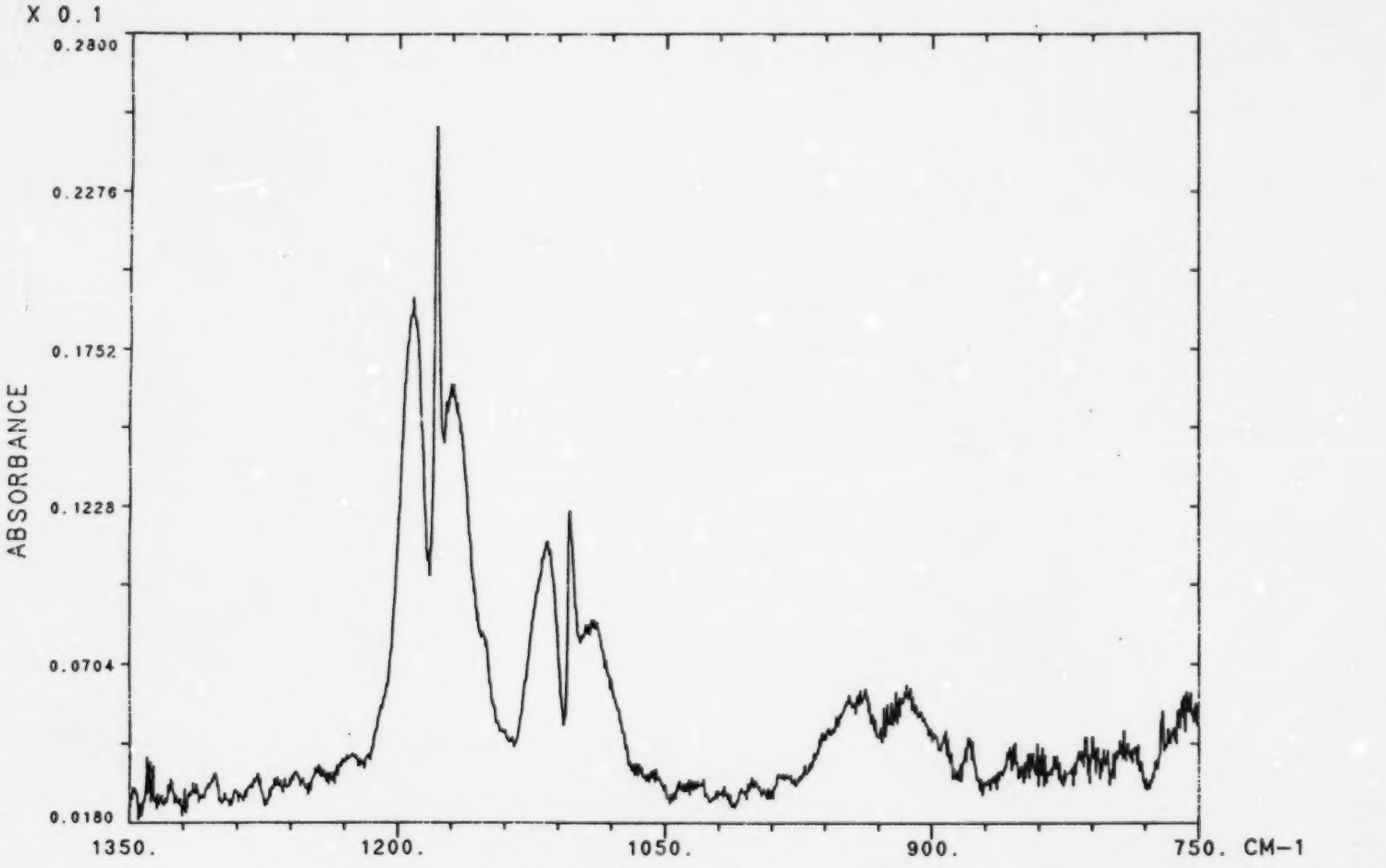

Figure C-75. Calibration of spectrometer for dimethyl ether at .1220 torr ? Lect. bot. Source 25 cm from aperture and 16 cm cell mirror 35 cm 740.0 torr.

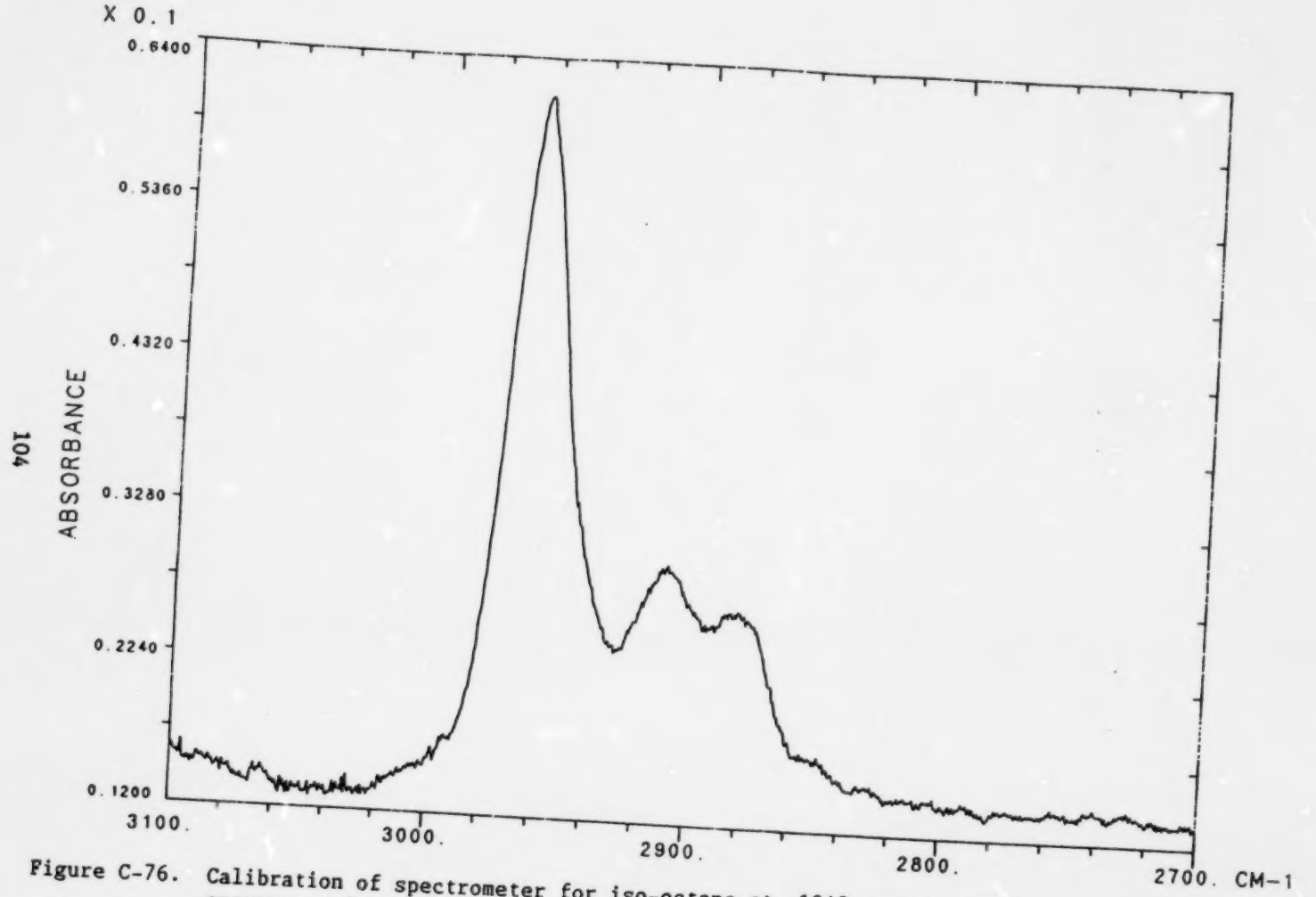

Figure C-76. Calibration of spectrometer for iso-octane at .1040 torr ? Lect. bot. Source 25 cm from aperture and 16 cm cell mirror 35 cm 740.0 torr.